Electronic Supplementary Material (ESI) for ChemComm.

Three-component reactions of isocyanoacetates, amines and 3-formylchromones initiated by an unexpected *aza*-Michael addition

Jia-Yu Liao, Wei Jie Yap, Ji'En Wu, Ming Wah Wong* and Yu Zhao*

Supporting Information

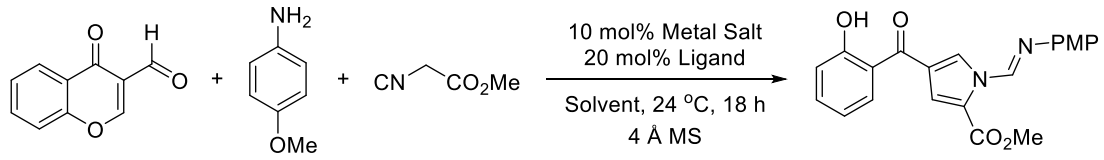
Table of Contents **Page**

I. General information

^{1}H and **^{13}C NMR** spectra were recorded on a Bruker AFC 300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: ^{1}H (chloroform δ 7.26; Acetone δ 2.05), ^{13}C (chloroform δ 77.0; Acetone δ 29.8, 206.3). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constants (Hz) and integration. For thin layer chromatography (**TLC**), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. High resolution mass spectra (**HRMS**) were obtained on a Finnigan/MAT 95XL-T spectrometer.

Unless otherwise noted, all the reactions were carried out open to air at ambient temperature. Dichloromethane, diethyl ether (Et_2O), tetrahydrofuran (THF), and toluene were dried over a Pure Solv solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received without further purification. Other chemicals including all the 3-formylchromones, amines, isocyanoacetates, metal salts and phosphine ligands were purchased from commercial suppliers and used as received without further purification. Imine **6** was prepared by condensing 3-formylchromone **1a** with *p*-anisidine **2a** using catalytic amount of *p*-toluenesulfonic acid (TsOH) under azeotropic removal of water.[1]

II. Optimization of reaction conditions[a]



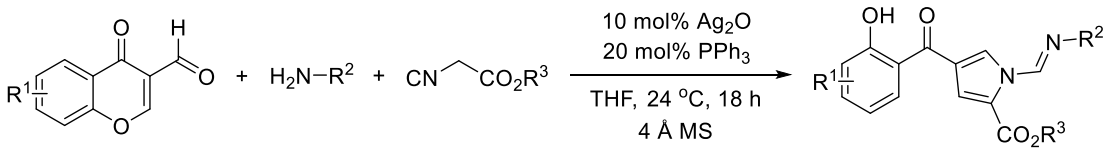
1a **2a** **3a** **5a**

Entry	Metal Salt	Ligand	Solvent	Yield (%)[b]
1	Ag_2O	/	THF	27
2	Ag_2CO_3	/	THF	17
3	Cu_2O	/	THF	6
4	$Cu(OAc)_2$	/	THF	16
5	Ag_2O	PPh_3	THF	37
6	Ag_2O	dppf	THF	21
7	Ag_2O	dppe	THF	17
8	Ag_2O	PPh_3	1,4-dioxane	35
9	Ag_2O	PPh_3	Et_2O	14
10	Ag_2O	PPh_3	toluene	23
11	Ag_2O	PPh_3	$CHCl_3$	19
12	Ag_2O	PPh_3	CH_2Cl_2	19
13[c]	Ag_2O	PPh_3	THF	53
14[c-d]	**Ag_2O**	**PPh_3**	**THF**	**70**

[a] The reactions were carried out under ambient atmosphere with 0.1 mmol of **1a**, 0.12 mmol of **2a** and 0.12 mmol of **3a** in 1 mL of the solvent. [b] Isolated yields. [c] 2 mL of THF was used. [d] 2.0 equiv of **2a** was used.

Note: The variation of other conditions such as reaction temperatures failed to afford a higher yield.

III. Ag-catalyzed three-component reactions

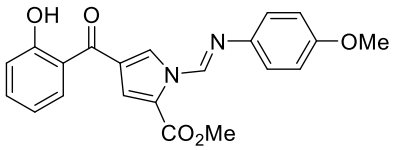


1 (1.0 equiv) **2** (2.0 equiv) **3** (1.2 equiv) **5**

General procedure. To a 10 mL vial charged with Ag_2O (2.3 mg, 0.010 mmol), PPh_3 (5.2 mg, 0.020 mmol) and 4 Å MS (30 mg) was added anhydrous THF (2.0 mL). The mixture was allowed to stir at ambient temperature for 5 min, then amine **2** (0.20 mmol) was added in one portion, followed by isocyanoacetate **3** (0.12 mmol) and 3-formylchromone **1** (0.10 mmol). The reaction mixture was allowed to stirred at ambient temperature for 18 h, concentrated and purified by flash chromatography (hexanes/ethyl acetate) to afford the product **5**.

IV. Characterization of compounds 5

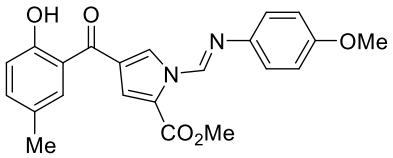
Methyl (*E*)-4-(2-hydroxybenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (5a)



5a

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 70% yield. **^{1}H NMR** (500 MHz, Acetone-d_6): δ 11.88 (s, 1H), 9.52 (s, 1H), 8.50 (d, *J* = 1.8 Hz, 1H), 8.02 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.62-7.56 (m, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.34-7.24 (m, 2H), 7.07-6.96 (m, 4H), 3.91 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, Acetone-d_6): δ 194.0, 163.3, 161.5, 159.7, 144.0, 141.3, 137.0, 132.7, 127.7, 125.2, 125.1, 123.6, 121.7, 120.9, 120.1, 118.9 115.5, 55.8, 52.5; **HRMS** (ESI): m/z calcd. for $[C_{21}H_{17}N_2O_5, M-H]^-$: 377.1143; Found: 377.1144.

Methyl (*E*)-4-(2-hydroxy-5-methylbenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (5b)

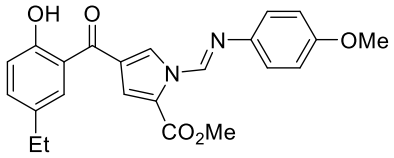


5b

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 55% yield. **^{1}H NMR** (500 MHz, Acetone-d_6): δ 11.66 (s, 1H), 9.52 (s, 1H), 8.50 (d, *J* = 1.8 Hz, 1H), 7.79 (d, *J* = 1.4 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.44-7.39 (m, 1H), 7.32-7.26 (m, 2H), 7.03-6.98 (m, 2H), 6.94 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 3.83 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (126 MHz,

Acetone-d_6): δ 194.0, 161.5, 161.2, 159.7, 144.1, 141.3, 137.9, 132.3, 129.2, 127.6, 125.3, 125.1, 123.6, 121.7, 120.7, 118.7, 115.5, 55.8, 52.5, 20.5; **HRMS** (ESI): m/z calcd. for [$C_{22}H_{19}N_2O_5$, M-H]$^-$: 391.1299; Found: 391.1294.

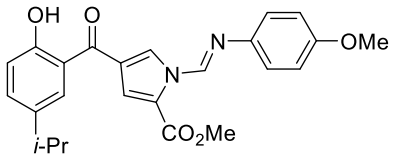
Methyl (*E*)-4-(5-ethyl-2-hydroxybenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (**5c**)



5c

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 49% yield. **^{1}H NMR** (500 MHz, Acetone-d_6): δ 11.65 (s, 1H), 9.53 (s, 1H), 8.51 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 2.1 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.46 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.32-7.27 (m, 2H), 7.04-6.99 (m, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H), 3.83 (s, 3H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, Acetone-d_6): δ 194.0, 161.5, 161.3, 159.7, 144.0, 141.3, 136.8, 135.7, 131.2, 127.7, 125.3, 125.1, 123.6, 121.6, 120.8, 118.8, 115.5, 55.8, 52.5, 28.5, 16.2; **HRMS** (ESI): m/z calcd. for [$C_{23}H_{21}N_2O_5$, M-H]$^-$: 405.1456; Found: 405.1461.

Methyl (*E*)-4-(2-hydroxy-5-isopropylbenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (**5d**)

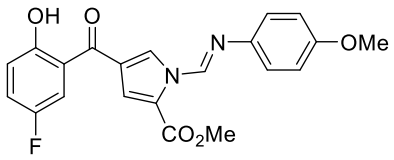


5d

The crude reaction mixture was purified by flash column chromatography

(hexanes/EtOAc 5:1). Yellow wax, 45% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.73 (s, 1H), 9.56 (s, 1H), 8.56 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 2.2 Hz, 1H), 7.54 (d, *J* = 1.9 Hz, 1H), 7.41 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.25-7.18 (m, 2H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.96-6.90 (m, 2H), 3.92 (s, 3H), 3.84 (s, 3H), 2.92 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 193.3, 161.0, 160.7, 158.6, 142.7, 140.2, 139.3, 134.5, 129.0, 127.2, 124.6, 123.7, 122.7, 121.7, 119.6, 118.2, 114.6, 55.5, 52.1, 33.2, 24.0; **HRMS** (ESI): m/z calcd. for $[C_{24}H_{23}N_2O_5, M\text{-}H]^-$: 419.1612; Found: 419.1623.

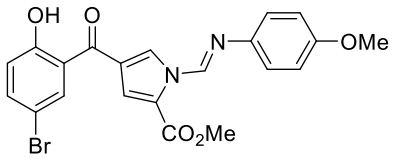
Methyl (*E*)-4-(5-fluoro-2-hydroxybenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (**5e**)



5e

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 46% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.68 (s, 1H), 9.54 (s, 1H), 8.55 (d, *J* = 1.8 Hz, 1H), 7.60 (dd, *J* = 8.9, 3.1 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.28-7.20 (m, 3H), 7.03 (dd, *J* = 9.1, 4.5 Hz, 1H), 6.96-6.90 (m, 2H), 3.92 (s, 3H), 3.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.3, 160.9, 158.8 (d, *J* = 1.3 Hz), 158.7, 154.9 (d, *J* = 238.6 Hz), 142.6, 140.1, 127.0, 124.0, 123.9, 123.5 (d, *J* = 23.6 Hz), 122.7, 121.5, 119.7 (d, *J* = 7.3 Hz), 119.4 (d, *J* = 6.3 Hz), 116.6 (d, *J* = 23.7 Hz), 114.6, 55.5, 52.1; **HRMS** (ESI): m/z calcd. for $[C_{21}H_{16}FN_2O_5, M\text{-}H]^-$: 395.1049; Found: 395.1049.

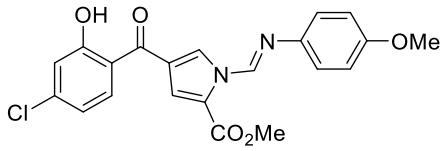
Methyl (*E*)-4-(5-bromo-2-hydroxybenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (**5f**)



5f

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 52% yield. **^{1}H NMR** (500 MHz, Acetone-d_6): δ 11.58 (s, 1H), 9.52 (s, 1H), 8.52 (d, *J* = 1.8 Hz, 1H), 8.04 (d, *J* = 2.5 Hz, 1H), 7.70 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.33-7.24 (m, 2H), 7.06-6.98 (m, 3H), 3.92 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, Acetone-d_6): δ 192.8, 161.7, 161.4, 159.8, 144.0, 141.3, 139.2, 134.5, 127.9, 125.3, 124.9, 123.7, 123.1, 121.4, 121.1, 115.5, 111.2, 55.8, 52.6; **HRMS** (ESI): m/z calcd. for [$C_{21}H_{16}BrN_2O_5$, M-H]$^-$: 455.0248; Found: 455.0252.

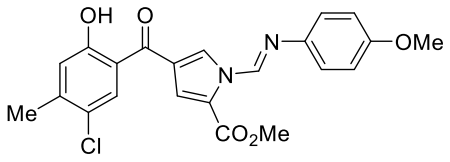
Methyl (*E*)-4-(4-chloro-2-hydroxybenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (5g)



5g

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 60% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.16 (s, 1H), 9.54 (s, 1H), 8.52 (s, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.52 (d, *J* = 1.7 Hz, 1H), 7.24-7.18 (m, 2H), 7.07 (s, 1H), 6.98-6.90 (m, 3H), 3.92 (s, 3H), 3.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.5, 163.4, 160.9, 158.7, 142.6, 141.9, 140.1, 132.6, 126.9, 124.2, 123.9, 122.7, 121.5, 119.7, 118.6, 118.4, 114.6, 55.5, 52.1; **HRMS** (ESI): m/z calcd. for [$C_{21}H_{16}ClN_2O_5$, M-H]$^-$: 411.0765; Found: 411.0766.

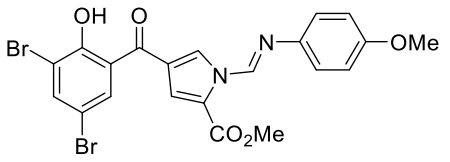
Methyl (*E*)-4-(5-chloro-2-hydroxy-4-methylbenzoyl)-1-(((4-methoxyphenyl)imino) methyl)-1*H*-pyrrole-2-carboxylate (5h)



5h

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 50% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.88 (s, 1H), 9.54 (s, 1H), 8.54 (d, *J* = 1.7 Hz, 1H), 7.86 (s, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.25-7.19 (m, 2H), 6.97-6.90 (m, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 192.0, 161.2, 160.9, 158.7, 145.3, 142.6, 140.2, 131.1, 126.9, 124.3, 124.1, 123.9, 122.8, 121.4, 120.5, 118.8, 114.6, 55.5, 52.1, 20.8; **HRMS** (ESI): m/z calcd. for $[C_{22}H_{18}ClN_2O_5, M\text{-}H]^-$: 425.0910; Found: 425.0912.

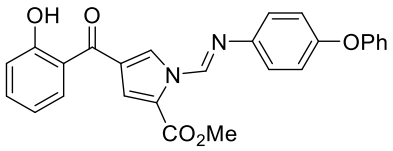
Methyl (*E*)-4-(3,5-dibromo-2-hydroxybenzoyl)-1-(((4-methoxyphenyl)imino)meth yl)-1*H*-pyrrole-2-carboxylate (5i)



5i

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 30% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.53 (s, 1H), 9.54 (s, 1H), 8.55 (s, 1H), 7.99 (d, *J* = 1.2 Hz, 1H), 7.90 (s, 1H), 7.50 (s, 1H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 3H), 3.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 191.8, 160.8, 158.8, 158.3, 142.4, 141.0, 139.9, 132.9, 127.4, 124.2, 123.4, 122.8, 121.5, 121.3, 114.6, 113.3, 110.5, 55.5, 52.2; **HRMS** (ESI): m/z calcd. for $[C_{21}H_{15}Br_2N_2O_5, M\text{-}H]^-$: 532.9353; Found: 532.9337.

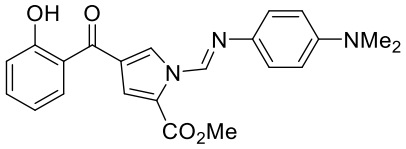
Methyl (*E*)-4-(2-hydroxybenzoyl)-1-(((4-phenoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (5j)



5j

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 48% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.96 (s, 1H), 9.56 (s, 1H), 8.55 (d, *J* = 1.5 Hz, 1H), 8.00-7.84 (m, 1H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.55-7.49 (m, 1H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.09-7.00 (m, 5H), 6.98 (t, *J* = 7.6 Hz, 1H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 193.3, 162.7, 161.0, 157.2, 156.1, 143.7, 142.6, 136.1, 131.7, 129.8, 127.0, 124.6, 123.8, 123.4, 122.8, 121.9, 119.9, 119.7, 119.0, 118.8, 118.5, 52.1; **HRMS** (ESI): m/z calcd. for $[C_{26}H_{21}N_2O_5, M+H]^+$: 441.1445; Found: 441.1448.

Methyl (*E*)-1-(((4-(dimethylamino)phenyl)imino)methyl)-4-(2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (5k)

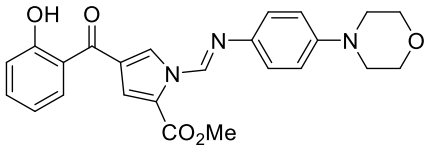


5k

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Brown wax, 69% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.00 (s, 1H), 9.56 (s, 1H), 8.56 (d, *J* = 1.8 Hz, 1H), 7.95 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.55 (d, *J* = 1.6 Hz, 1H), 7.53-7.49 (m, 1H), 7.26-7.20 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.98 (q, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H), 2.99 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 193.4, 162.7, 161.0, 140.9, 135.9, 131.7, 127.0, 124.2, 123.6,

122.8, 121.6, 120.0, 119.0, 118.4, 113.0, 52.0, 40.7; **HRMS** (ESI): m/z calcd. for $[C_{22}H_{22}N_3O_4, M+H]^+$: 392.1605; Found: 392.1610.

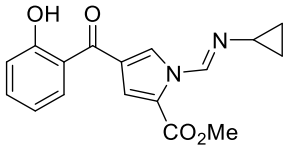
Methyl (*E*)-4-(2-hydroxybenzoyl)-1-(((4-morpholinophenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (**5l**)



5l

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 1:1). Yellow wax, 65% yield. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.98 (s, 1H), 9.56 (s, 1H), 8.55 (d, *J* = 1.7 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.55 (d, *J* = 1.8 Hz, 1H), 7.51 (dd, *J* = 11.3, 4.2 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.01-6.90 (m, 3H), 3.92 (s, 3H), 3.90-3.82 (m, 4H), 3.24-3.12 (m, 4H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 193.3, 162.7, 161.0, 142.3, 136.0, 131.7, 127.0, 124.4, 123.7, 122.6, 121.7, 119.9, 119.0, 118.4, 116.2, 66.8, 52.0, 49.3; **HRMS** (ESI): m/z calcd. for $[C_{24}H_{22}N_3O_5, M-H]^-$: 432.1565; Found: 432.1569.

Methyl (*E*)-1-((cyclopropylimino)methyl)-4-(2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (**5p**)

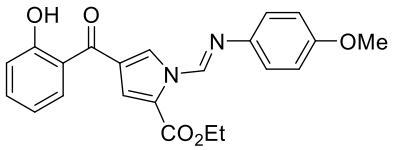


5p

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 10:1). Pale yellow wax, 23% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 11.97 (s, 1H), 9.41 (s, 1H), 8.27 (d, *J* = 1.9 Hz, 1H), 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H),

7.60-7.39 (m, 2H), 7.04 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.99-6.88 (m, 1H), 3.90 (s, 3H), 3.21-2.98 (m, 1H), 0.96-0.80 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 193.4, 162.6, 161.0, 143.3, 135.9, 131.7, 127.1, 123.9, 123.0, 121.1, 119.9, 118.9, 118.4, 52.0, 37.1, 8.5; **HRMS** (ESI): m/z calcd. for $[C_{17}H_{15}N_2O_4, M-H]^-$: 311.1044; Found: 311.1046.

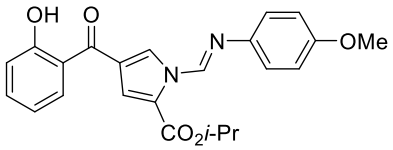
Ethyl (*E*)-4-(2-hydroxybenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (**5q**)



5q

The crude reaction mixture was purified by flash column chromatography (hexanes/EtOAc 5:1). Yellow wax, 69% yield. **^{1}H NMR** (500 MHz, Acetone-d_6): δ 11.87 (s, 1H), 9.53 (s, 1H), 8.50 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 11.2, 4.3 Hz, 1H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.32-7.22 (m, 2H), 7.08-6.96 (m, 4H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, Acetone-d_6): δ 194.1, 163.3, 161.0, 159.7, 144.1, 141.3, 136.9, 132.7, 127.6, 125.5, 125.1, 123.6, 121.6, 121.0, 120.1, 118.9, 115.5, 61.9, 55.8, 14.5; **HRMS** (ESI): m/z calcd. for $[C_{22}H_{21}N_2O_5, M+H]^+$: 393.1445; Found: 393.1450.

Isopropyl (*E*)-4-(2-hydroxybenzoyl)-1-(((4-methoxyphenyl)imino)methyl)-1*H*-pyrrole-2-carboxylate (**5r**)



5r

The crude reaction mixture was purified by flash column chromatography

(hexanes/EtOAc 5:1). Yellow wax, 62% yield. **^{1}H NMR** (500 MHz, Acetone-d_6): δ 11.87 (s, 1H), 9.55 (s, 1H), 8.50 (d, *J* = 1.6 Hz, 1H), 8.02 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.67-7.57 (m, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.32-7.24 (m, 2H), 7.12-6.93 (m, 4H), 5.23 (dt, *J* = 12.5, 6.2 Hz, 1H), 3.83 (s, 3H), 1.38 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (126 MHz, Acetone-d_6): δ 194.1, 163.3, 160.6, 159.7, 144.2, 141.4, 136.9, 132.7, 127.6, 125.8, 125.1, 123.6, 121.5, 121.0, 120.1, 118.9, 115.5, 69.8, 55.8, 22.1; **HRMS** (ESI): m/z calcd. for $[C_{23}H_{23}N_2O_5, M+H]^+$: 407.1601; Found: 407.1607.

V. X-ray crystallographic analysis of 5a

The conformation of **5a** was determined by X-ray crystallographic analysis of a single crystal of **5a** (Figure S1). The crystal was prepared from the solution of **5a** in hexanes/ethyl acetate at 0 °C.

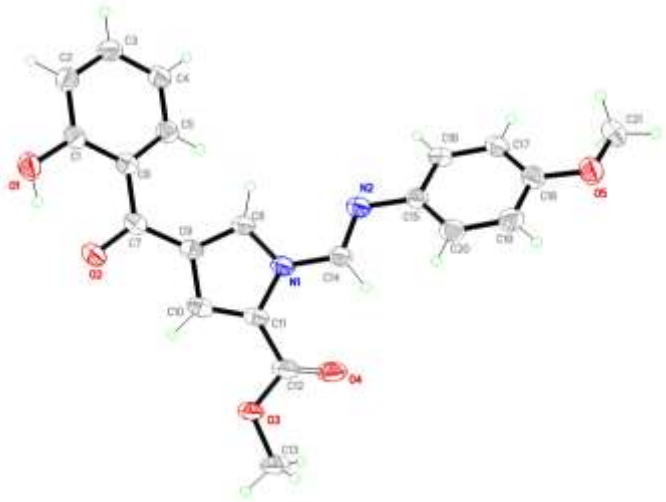


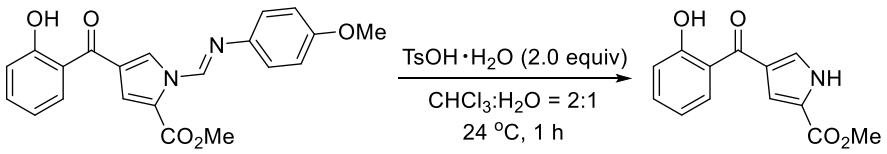
Figure S1. X-ray structure of **5a**

Table S1. Crystal data and structure refinement for F050

Identification code	F050	
Empirical formula	$C_{25}H_{27}N_2O_{5.25}$	
Formula weight	439.48	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 3.8268(2) Å	α = 90°
	b = 31.4297(12) Å	β = 92.2510(10)°
	c = 17.1304(7) Å	γ = 90°
Volume	2058.77(16) $Å^3$	

Z	4
Density (calculated)	1.418 Mg/m^3
Absorption coefficient	0.817 mm^{-1}
F(000)	932
Crystal size	0.360 x 0.260 x 0.160 mm^3
Theta range for data collection	2.812 to 68.231°
Index ranges	-4<=h<=4, -37<=k<=37, -20<=l<=20
Reflections collected	31351
Independent reflections	3774 [R(int) = 0.0382]
Completeness to theta = 67.679°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.6531
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3774 / 9 / 288
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0819, wR2 = 0.2745
R indices (all data)	R1 = 0.0870, wR2 = 0.2815
Extinction coefficient	n/a
Largest diff. peak and hole	1.013 and -0.653 $e.Å^{-3}$

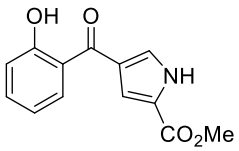
VI. Cleavage of the aldimine moiety in 5a



5a **7**

p-Toluenesulfonic acid monohydrate (79.4 mg, 0.42 mmol) was added to the mixture of **5a** (79.0 mg, 0.21 mmol), $CHCl_3$ (2 mL) and H_2O (1 mL). The reaction mixture was stirred at ambient temperature for 1 h, then was extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4), concentrated, and the residue was purified by flash chromatography (hexanes/ethyl acetate 3:1) to yield 45 mg of **7**.

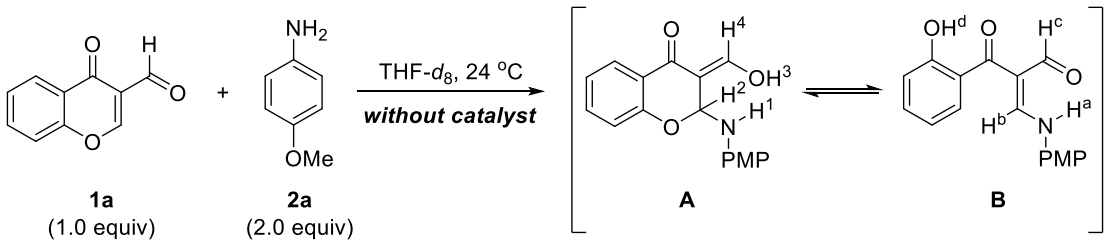
Methyl 4-(2-hydroxybenzoyl)-1*H*-pyrrole-2-carboxylate (**7**, known compound[2])



7

Pale yellow solid, 88% yield. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 12.04 (s, 1H), 10.17 (s, 1H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 (d, *J* = 1.5 Hz, 1H), 7.53-7.43 (m, 1H), 7.37 (d, *J* = 1.5 Hz, 1H), 7.04 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.99-6.85 (m, 1H), 3.91 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 193.6, 162.5, 161.4, 135.6, 131.7, 127.9, 125.1, 123.8, 120.0, 118.8, 118.3, 116.7, 52.0.

VII. Observation of intermediates



1a (1.0 equiv) **2a** (2.0 equiv) **A** **B**

A mixture of two unexpected intermediates **A** and **B** (tautomers to each other) were detected immediately after **1a** and **2a** were mixed together without catalyst, which were determined by NMR analysis to be the *aza*-Michael addition products. The structure of **A** was determined by the NOE correlation between H^1-H^2 and H^3-H^4 (Figure S2, in red box), and the structure of **B** was determined by the NOE correlation between H^a-H^b and H^b-H^c (Figure S2, in green box).

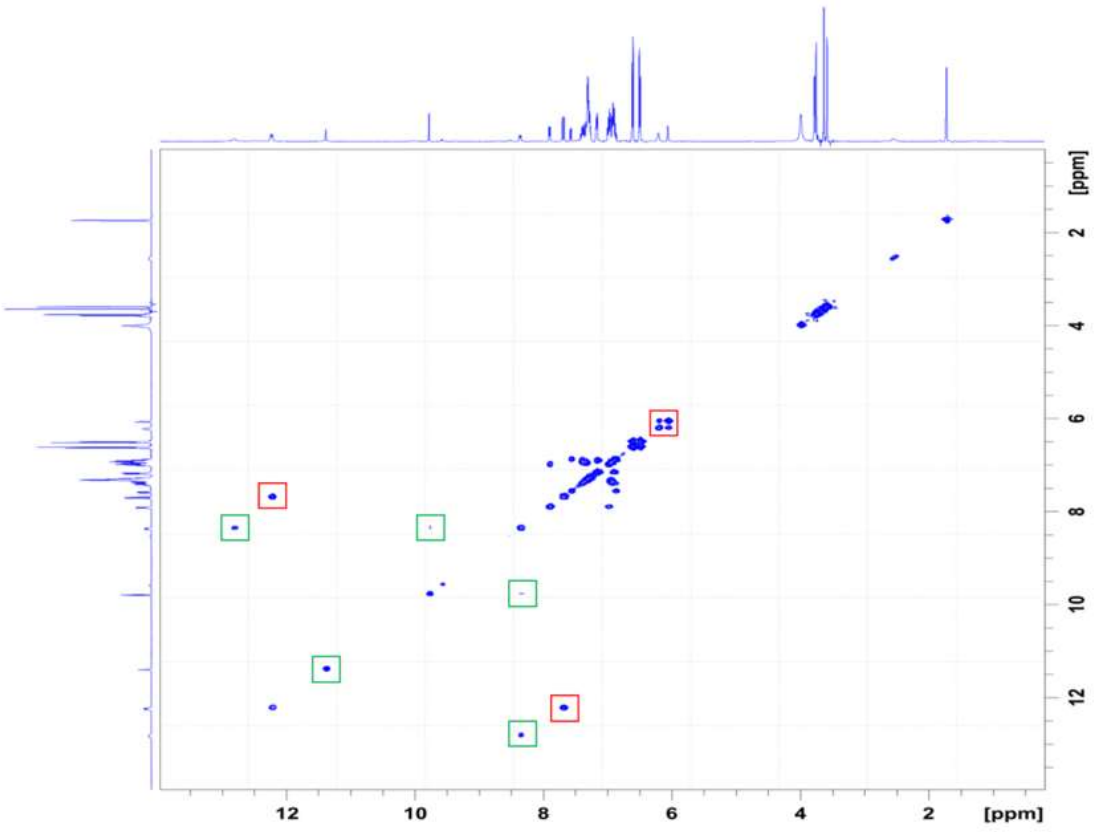
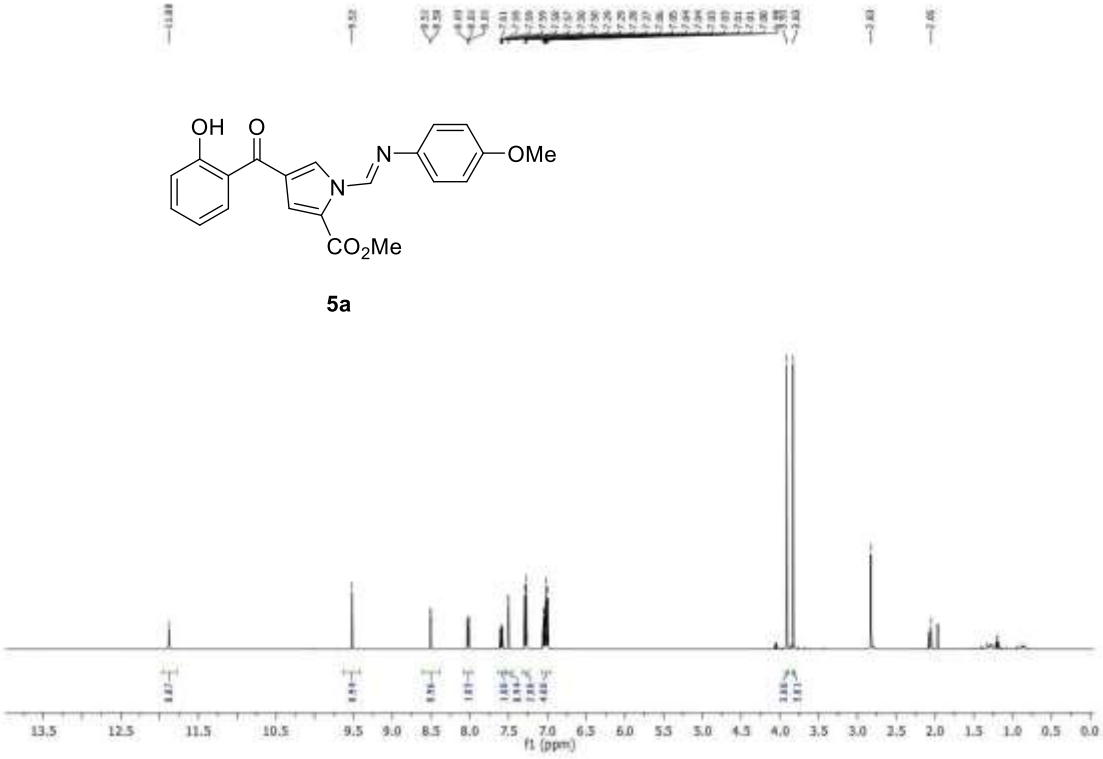
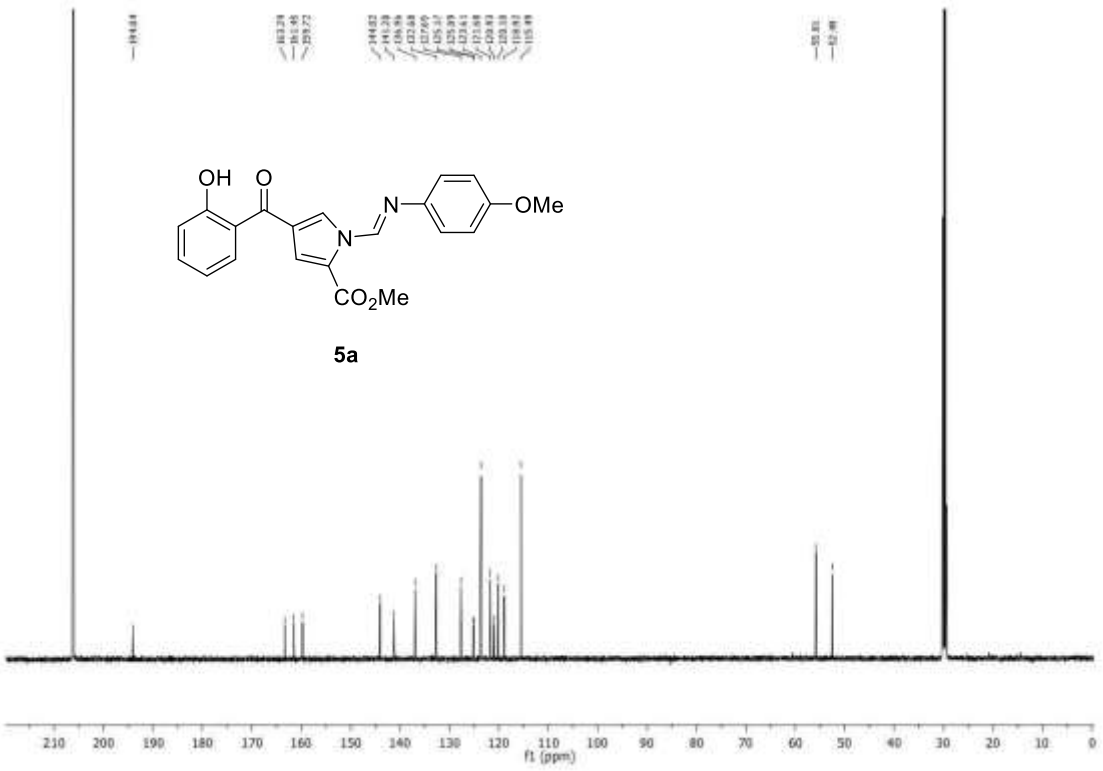


Figure S2. NOESY spectrum of intermediates **A** and **B**

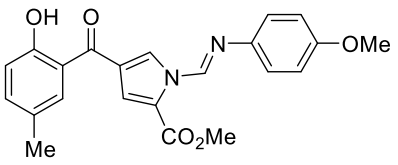
VIII. NMR spectra of the products



5a



5a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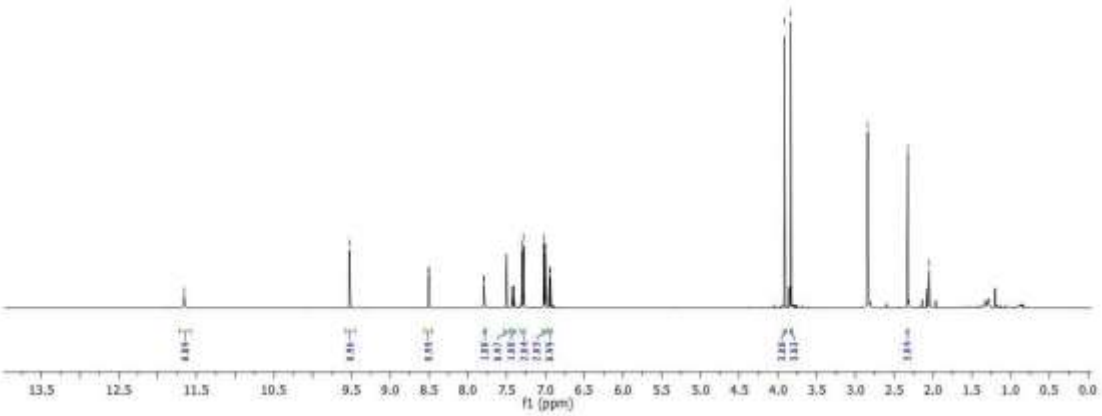
N
Me
CO2Me

5b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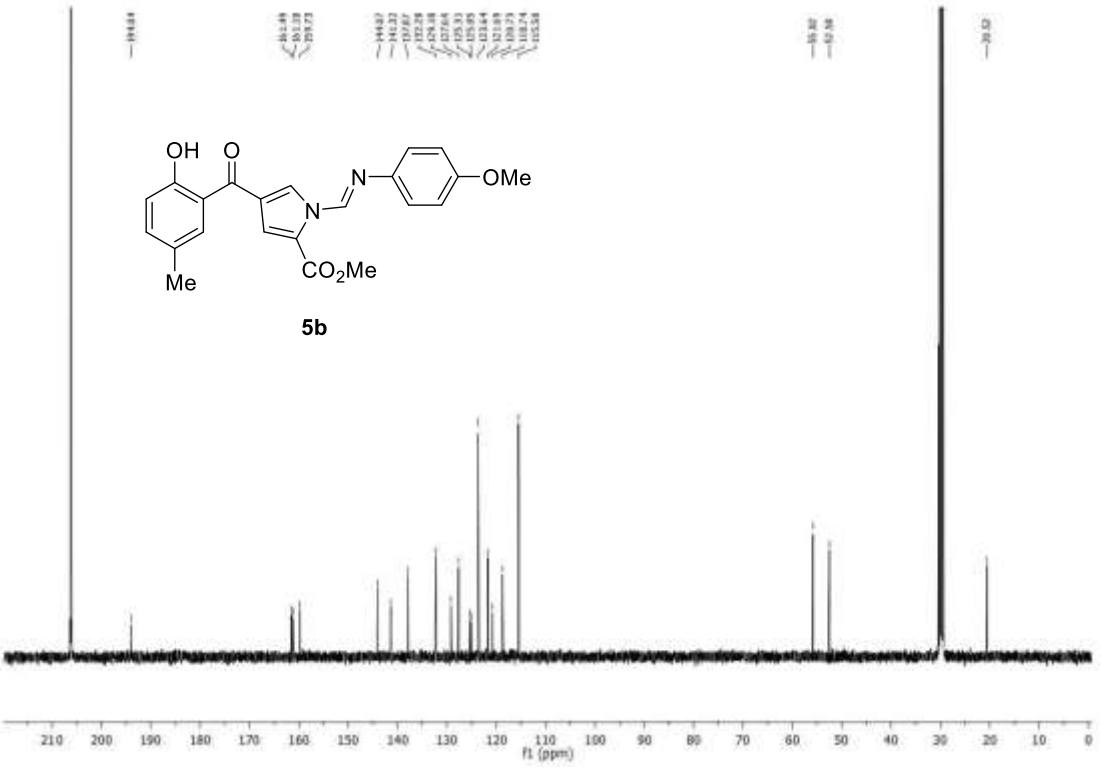
f1 (ppm)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CO2Me
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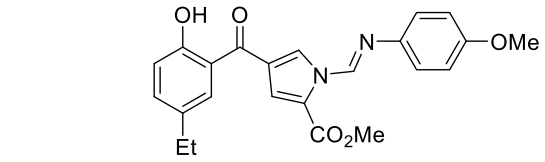
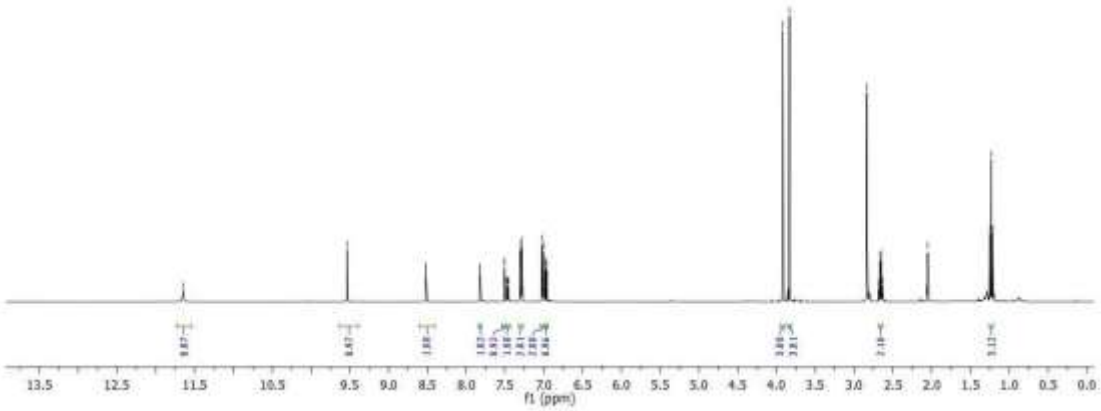
40
30
20
10
0
f1 (ppm)

5b


OH
O
N
OMe
N
CO2Me
Et

5c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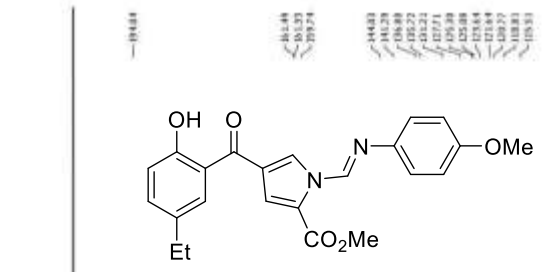
0.0
f1 (ppm)


OH
O
N
OMe
N
CO2Me
Et

5c

210
200
190
180
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150
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130
120
110
100
90
80
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50
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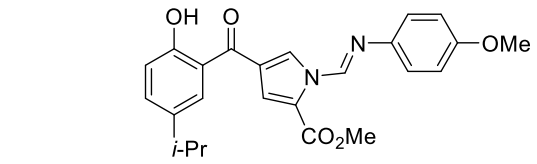
30
20
10
0
f1 (ppm)



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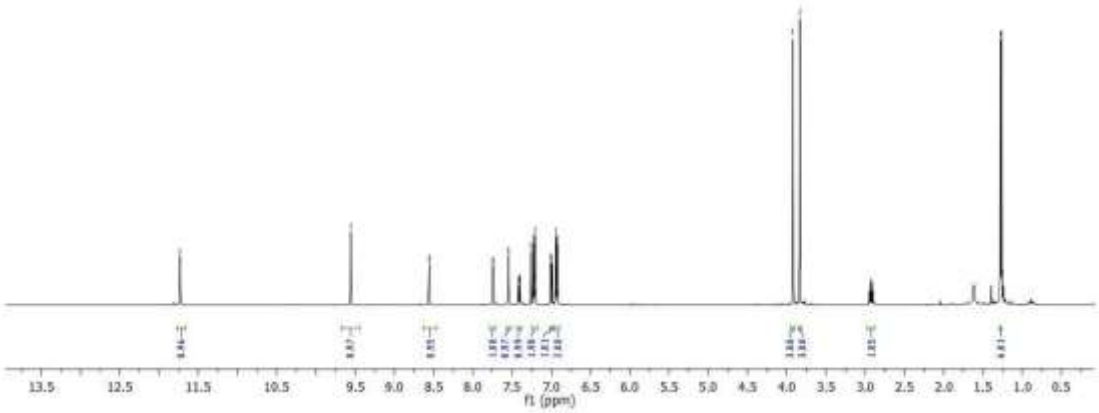

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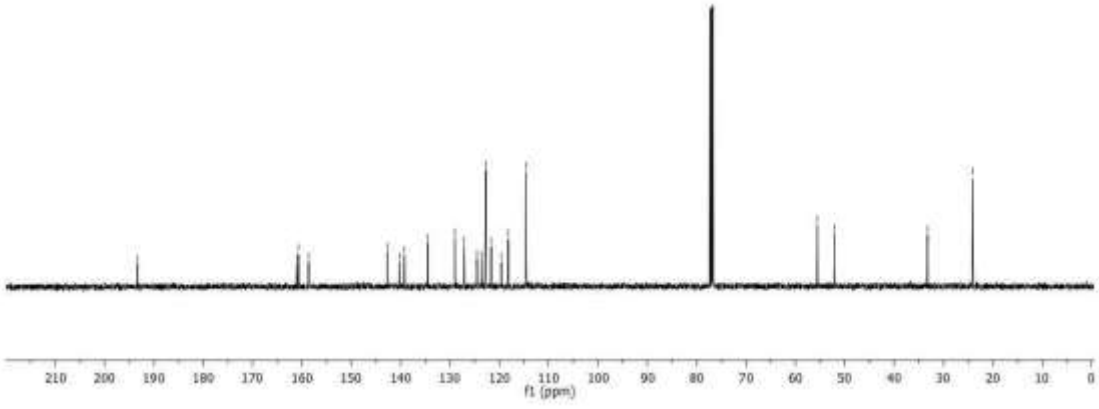

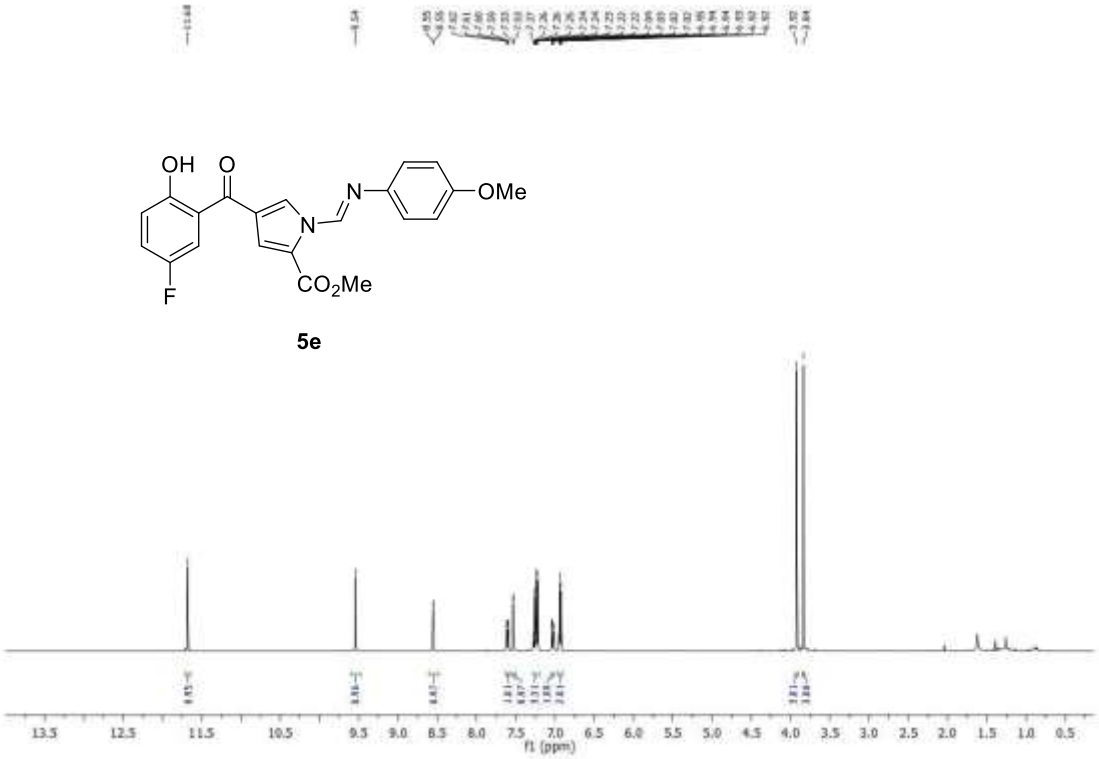
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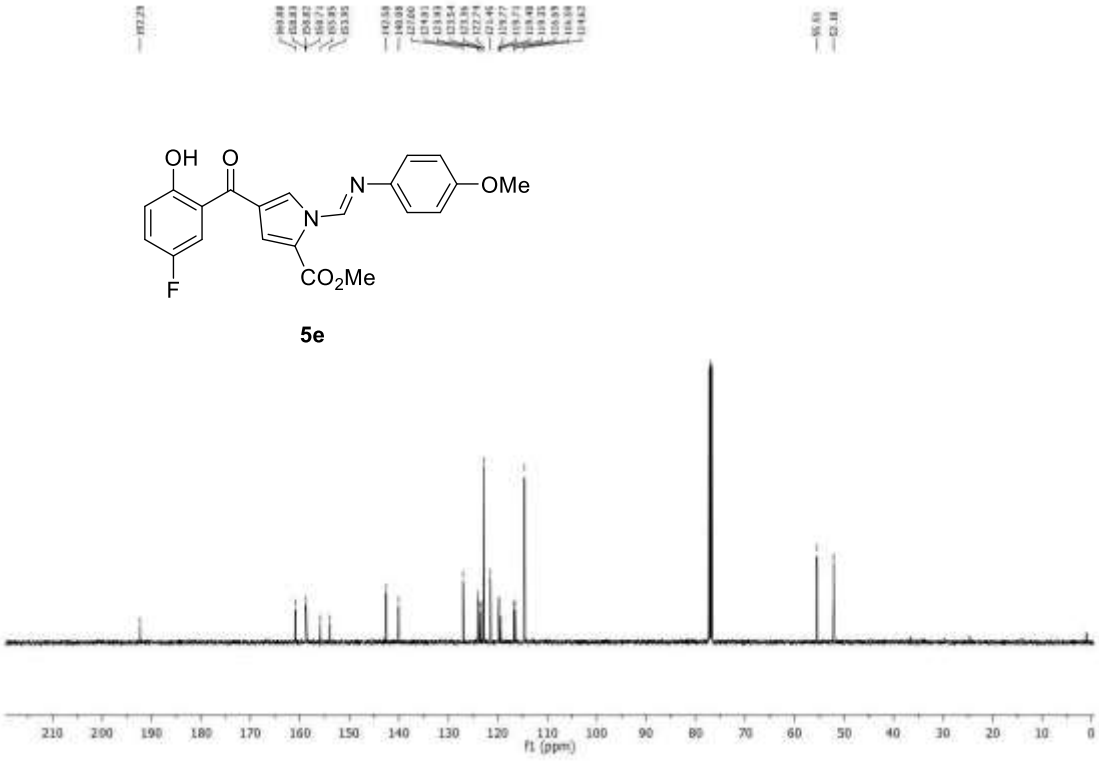
f1 (ppm)

5e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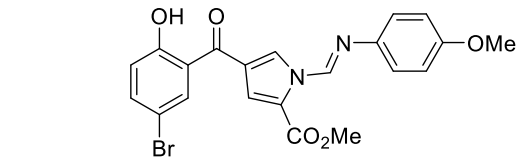
0
f1 (ppm)

5e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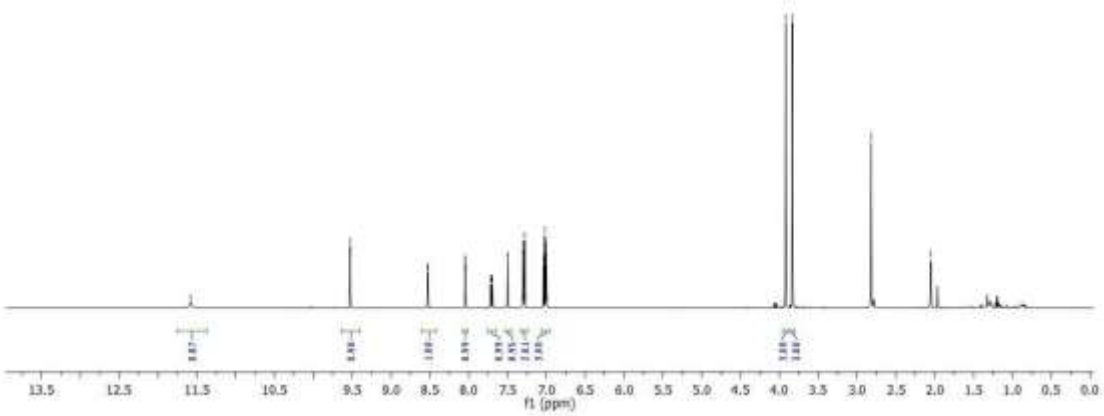
O
N
OMe
N
CO2Me
Br

5f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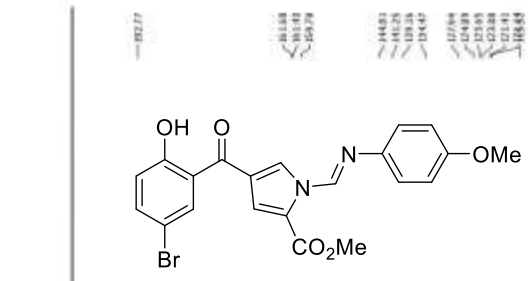
f1 (ppm)


OH
O
N
OMe
N
CO2Me
Br

5f

210
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180
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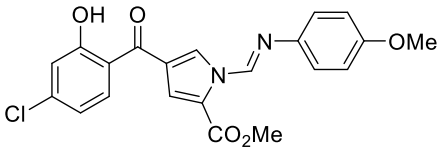
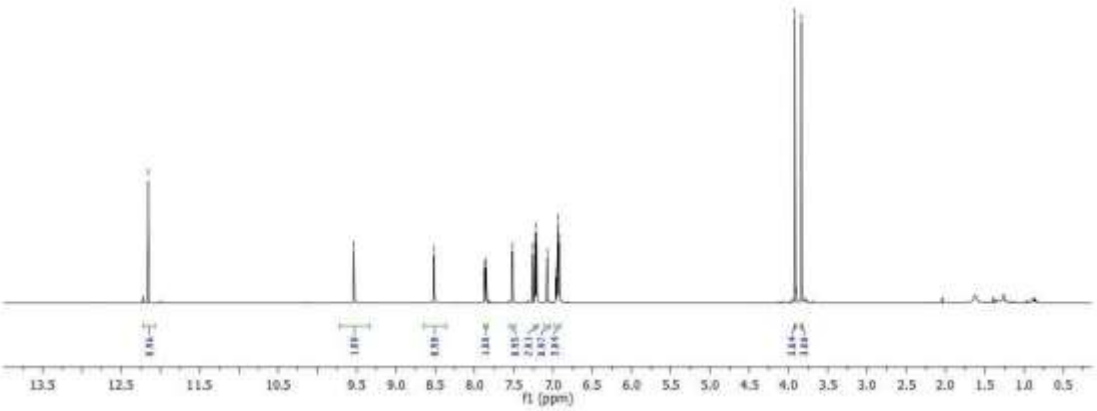
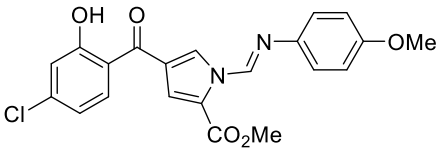
0
f1 (ppm)



5g





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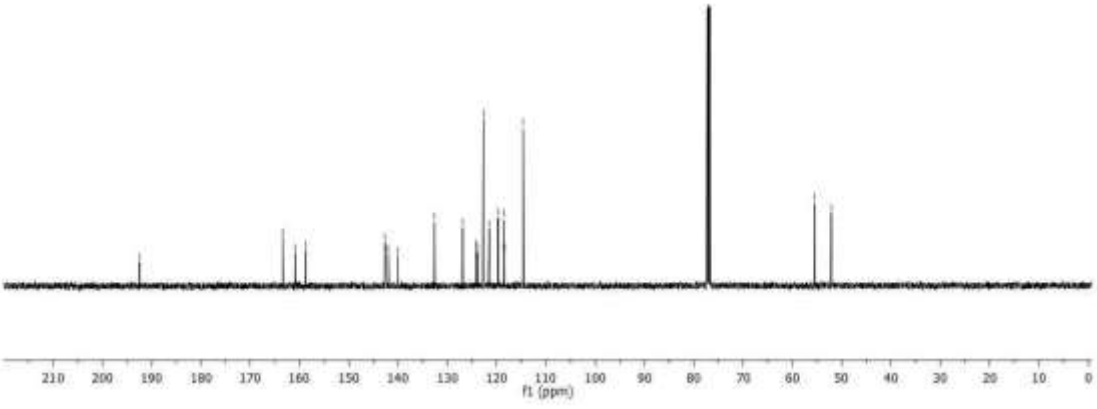

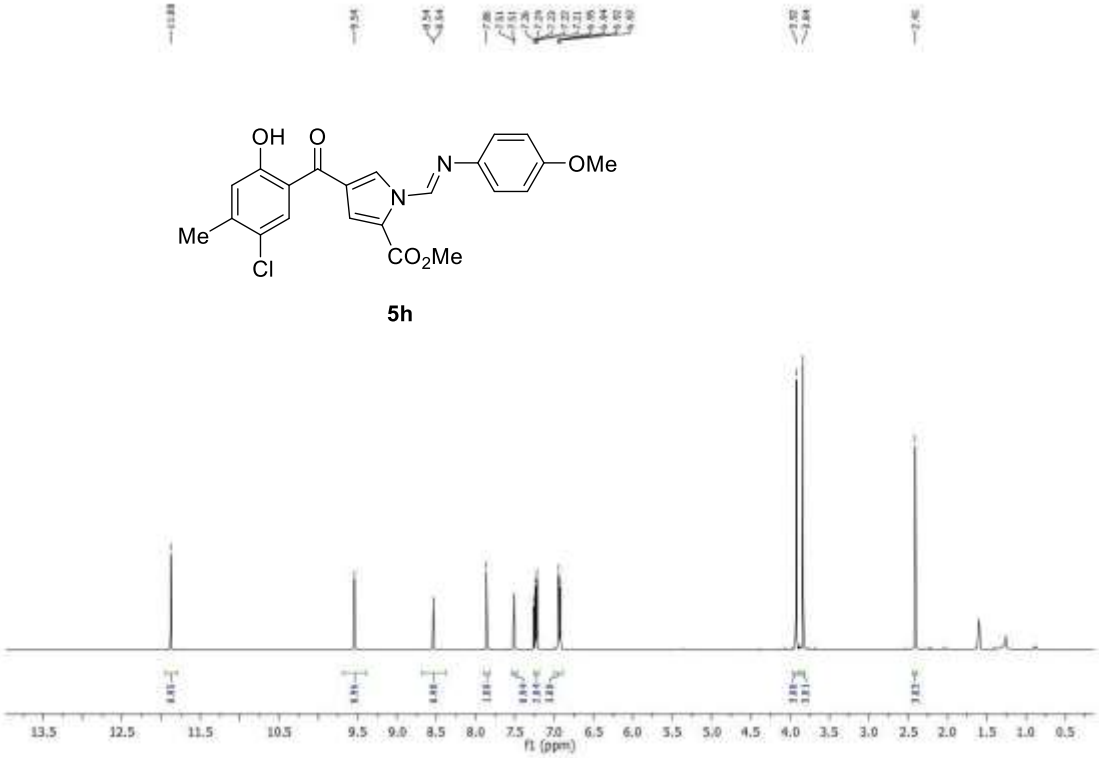
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Me
Cl
CO2Me
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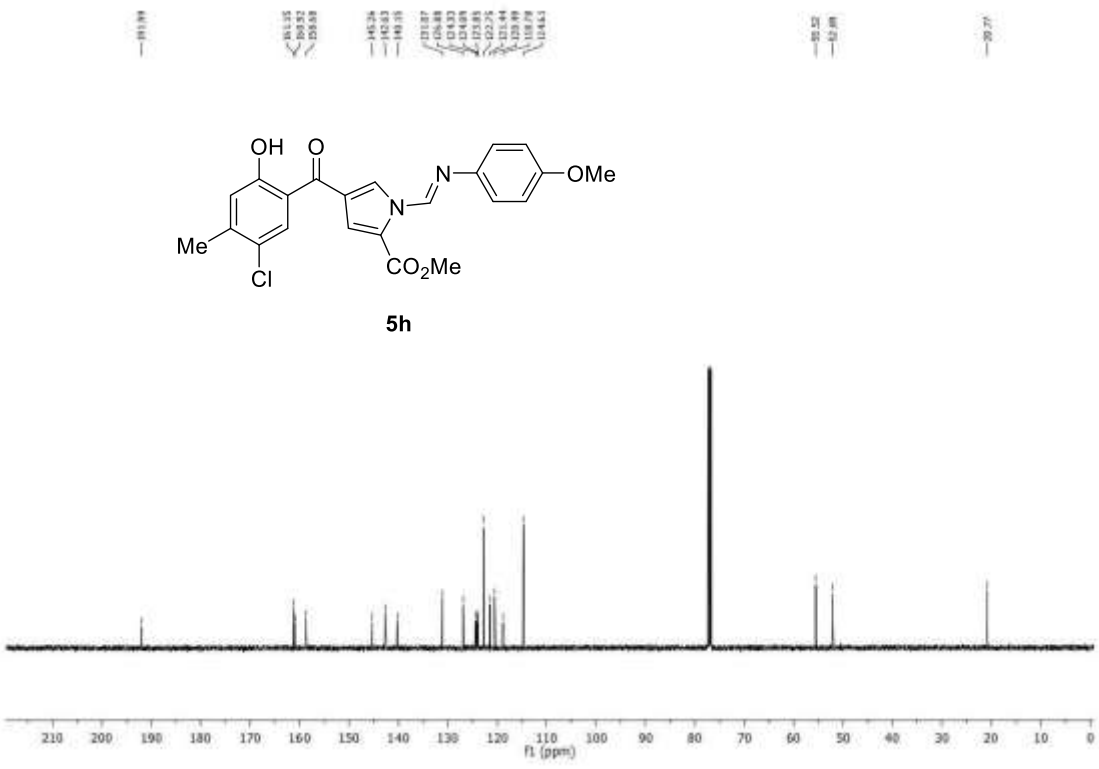
f1 (ppm)

5h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N
OMe
Me
Cl
CO2Me
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170
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80
70
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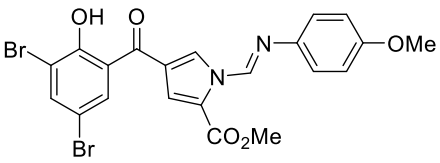
40
30
20
10
0
f1 (ppm)

5h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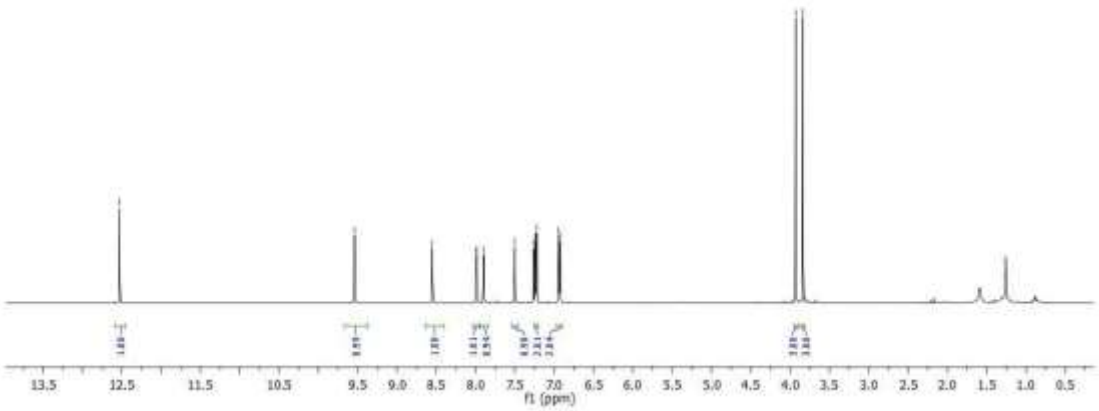
O
Br
N
OMe
N
CO2Me
Br

5i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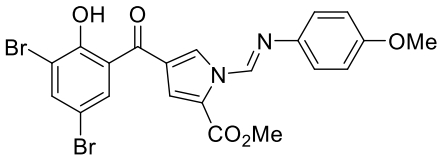
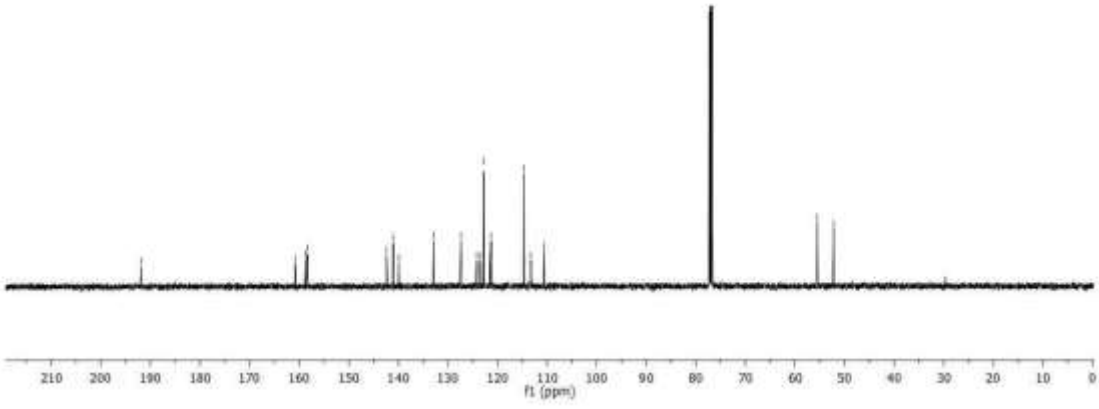
0.5
f1 (ppm)


OH
O
Br
N
OMe
N
CO2Me
Br

5i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10
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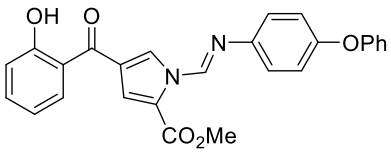
f1 (ppm)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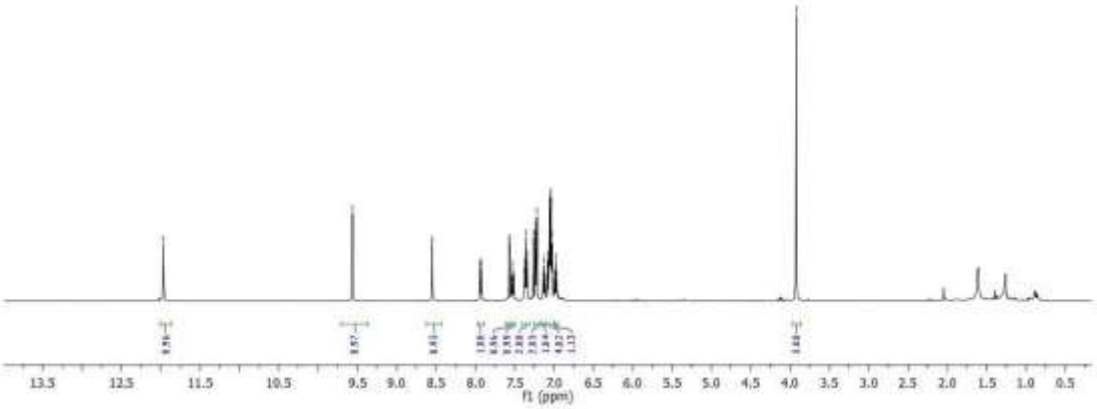
OPh
N
CO2Me

5j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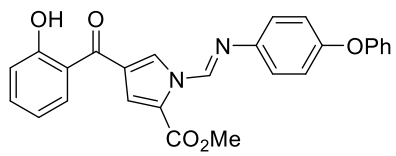
0.5
f1 (ppm)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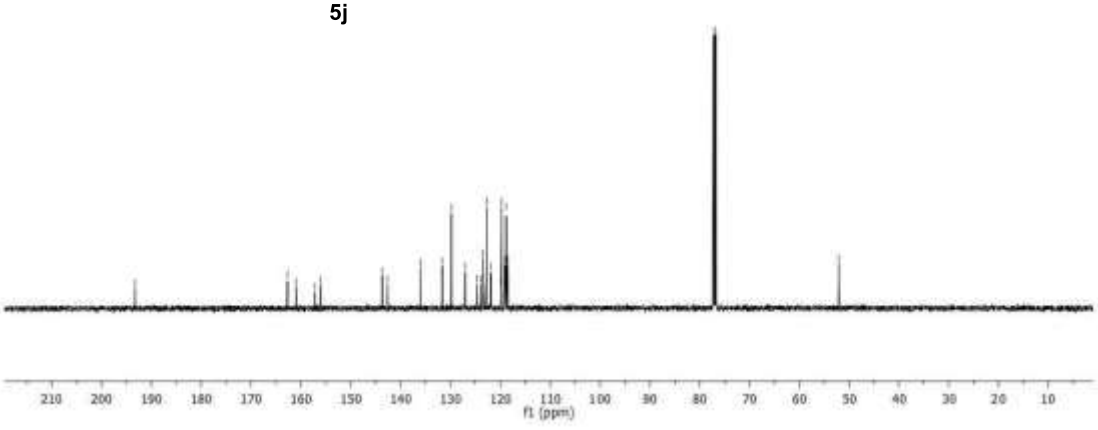
5j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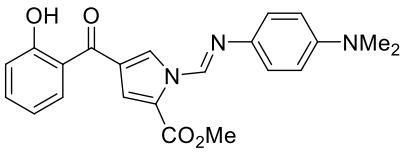
f1 (ppm)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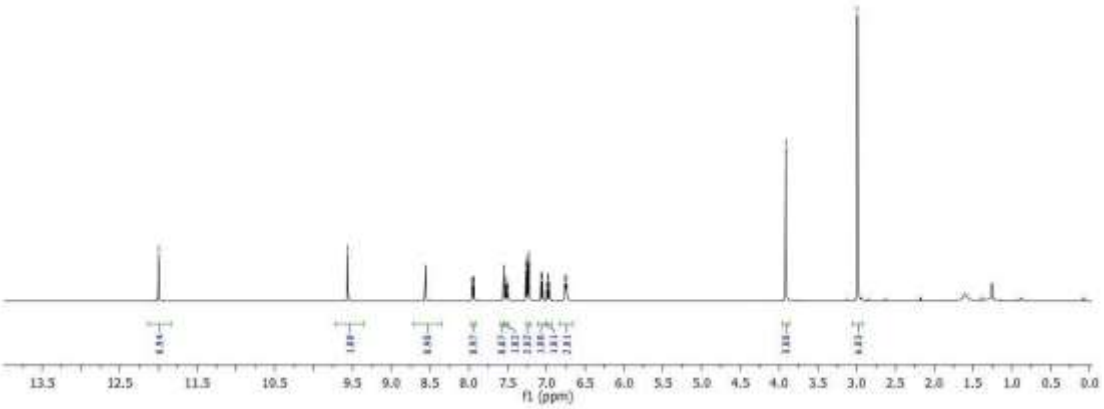
CO2Me

5k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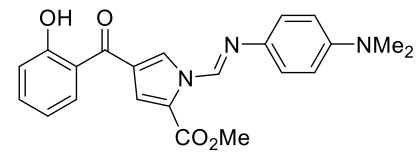
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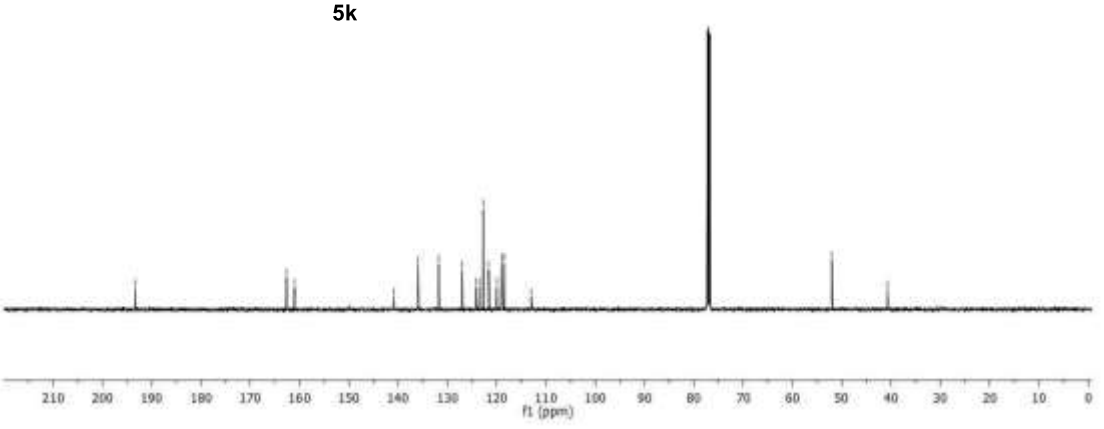
5k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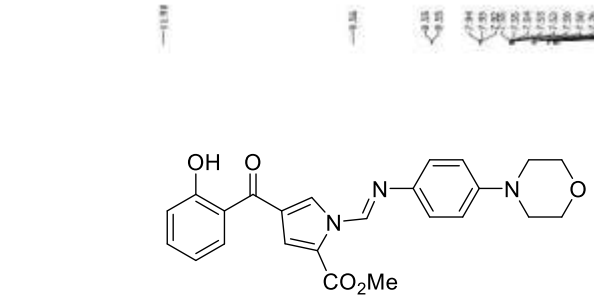
f1 (ppm)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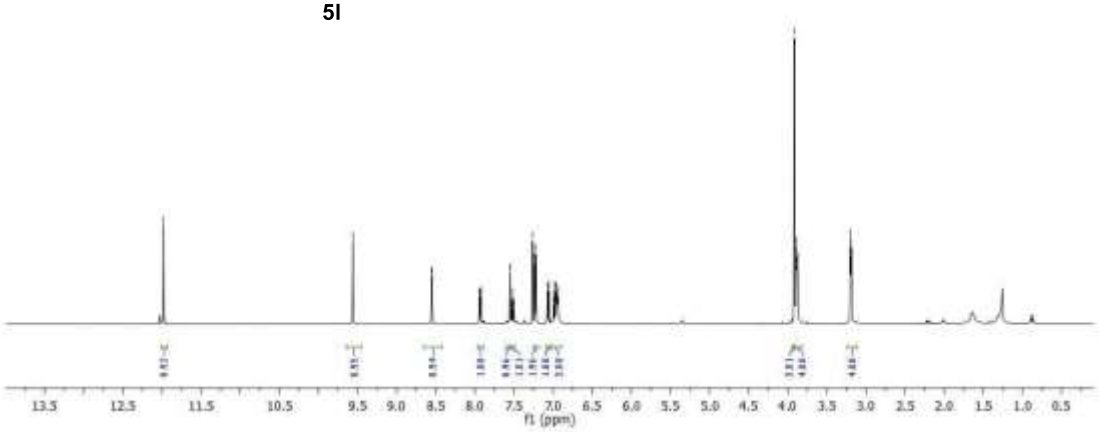
5l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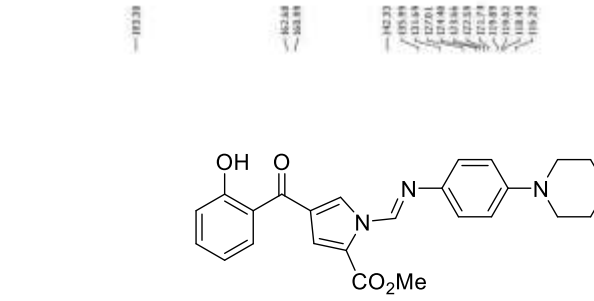
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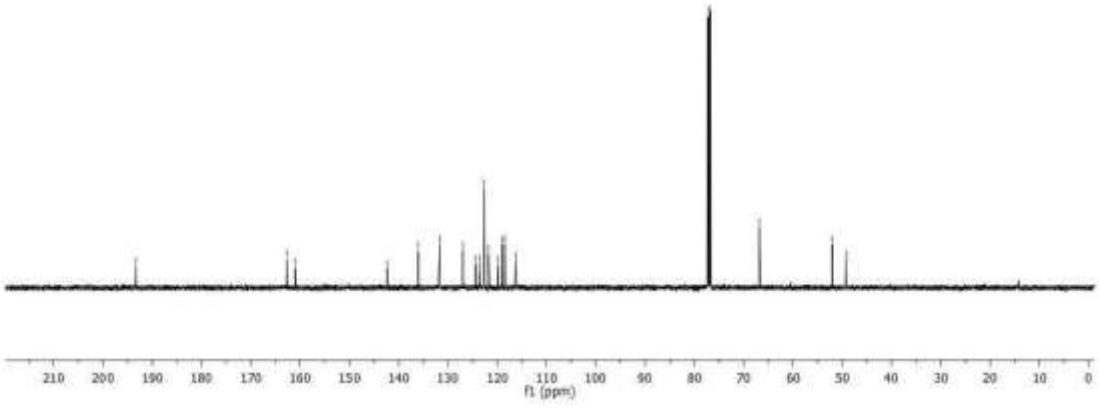
5l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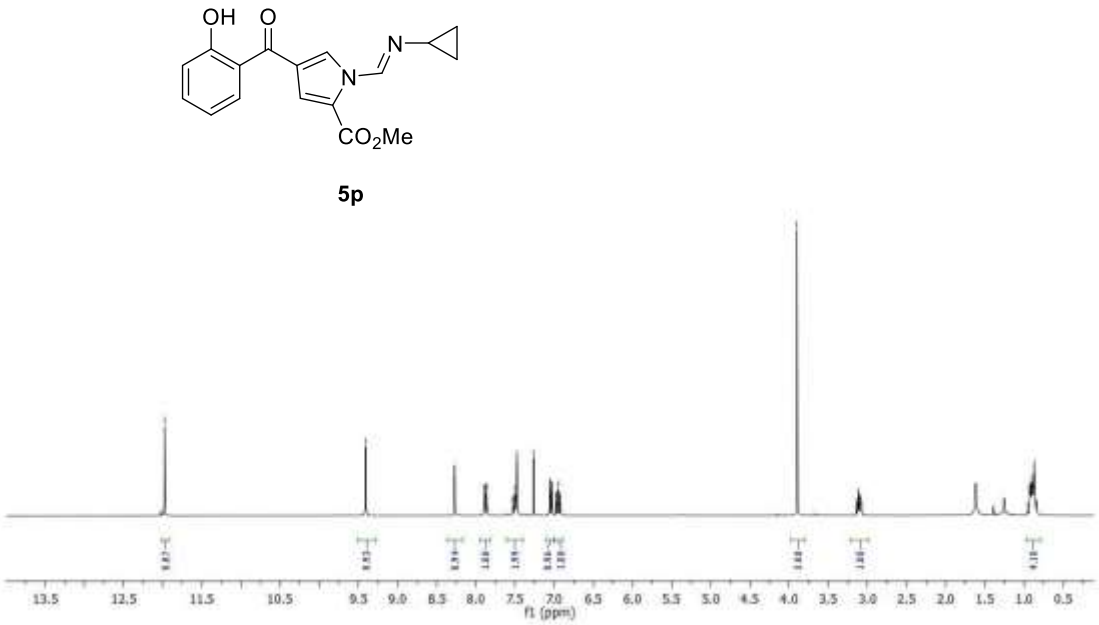
f1 (ppm)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8.5
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6.5
6.0
5.5
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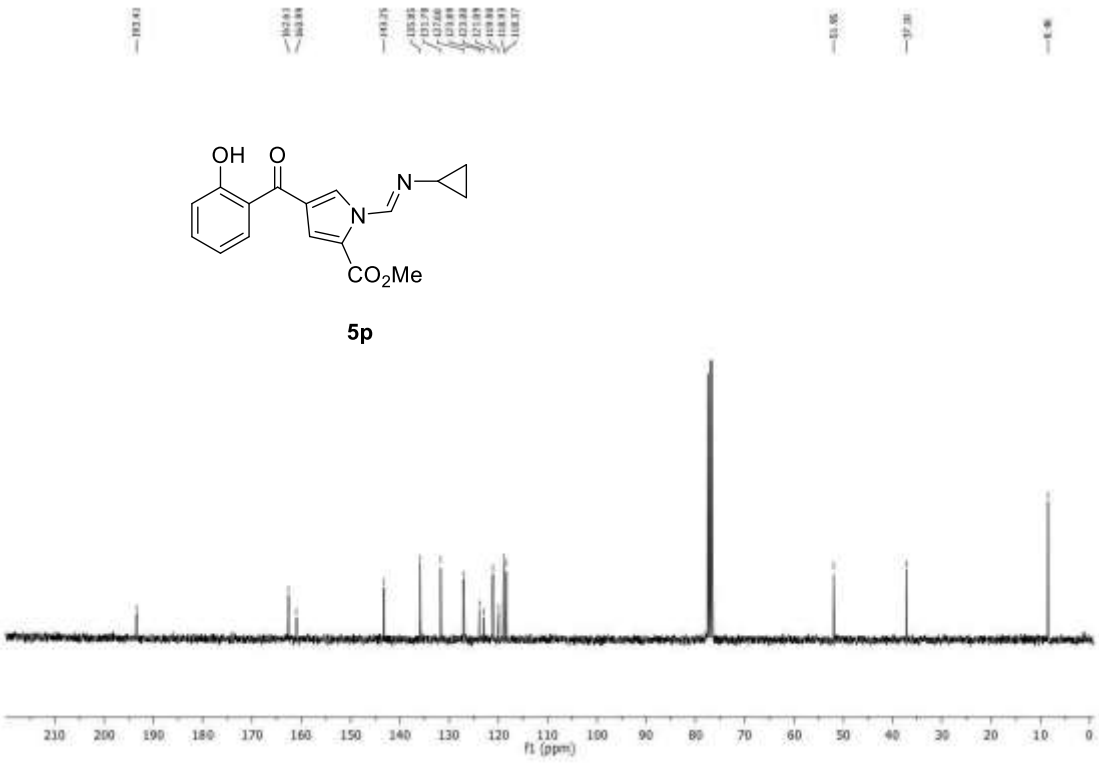
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

5p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N
CO2Me
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180
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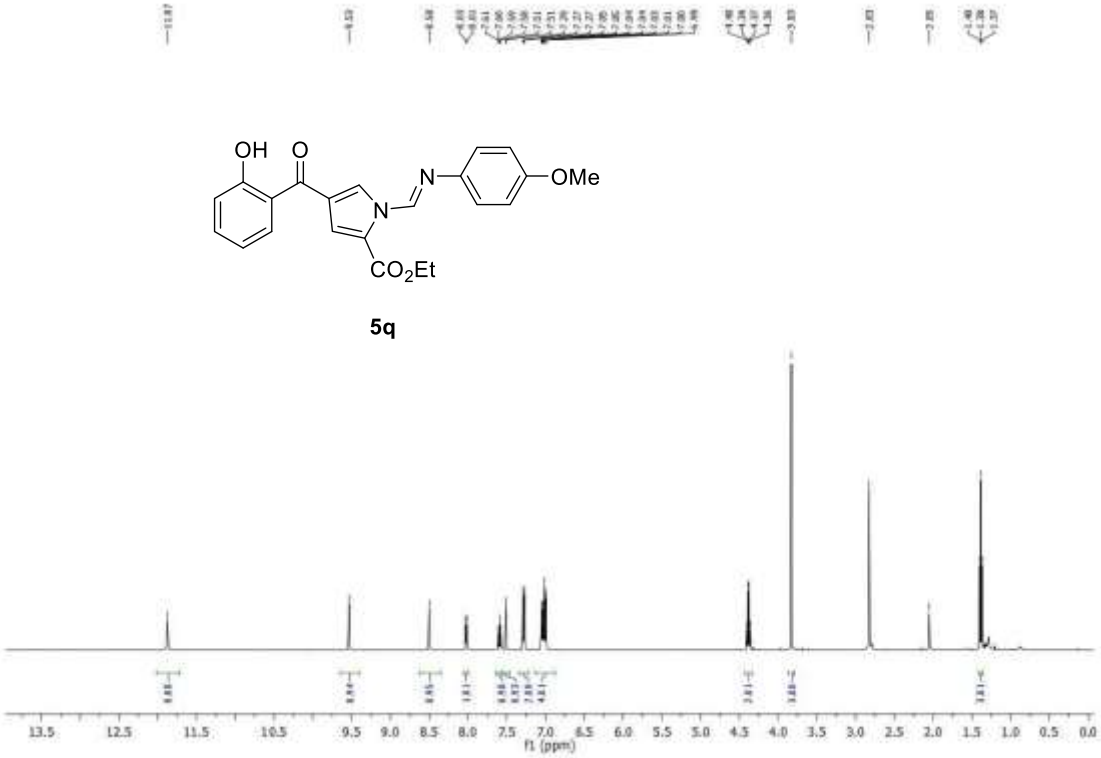
60
50
40
30
20
10
0
f1 (ppm)

5p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OMe
N
CO2Et
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9.0
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7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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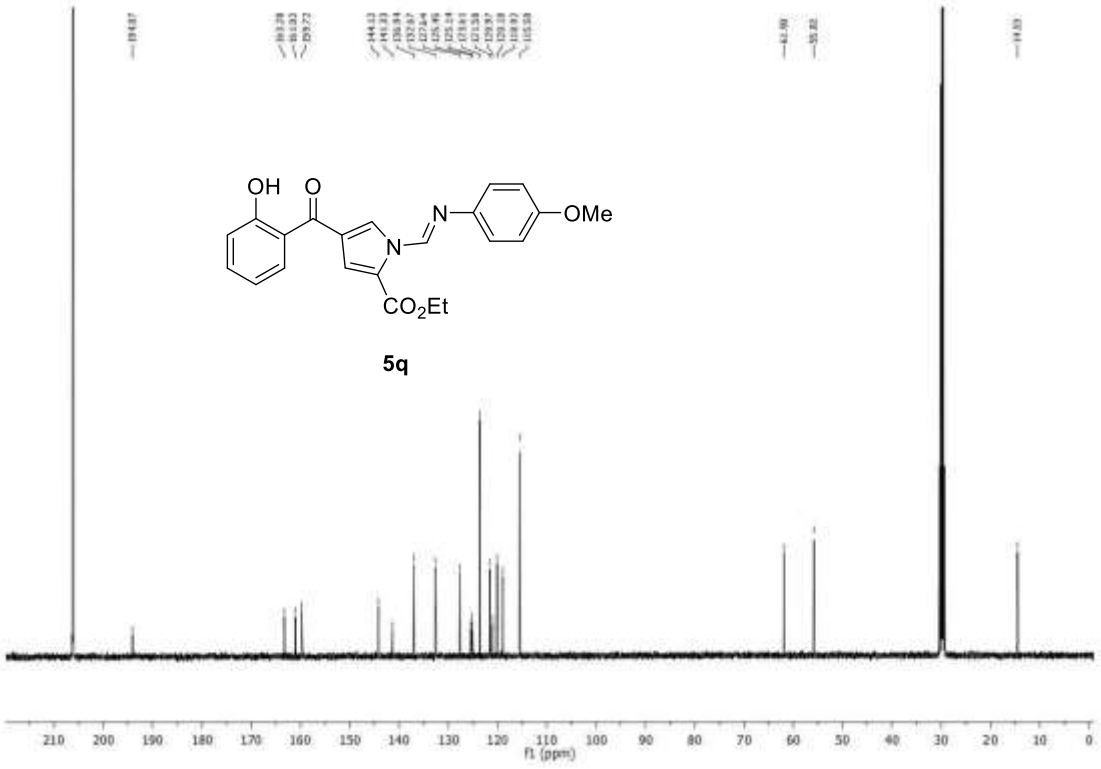
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5q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N
OMe
N
CO2Et
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200
190
180
170
160
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100
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80
70
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40
30
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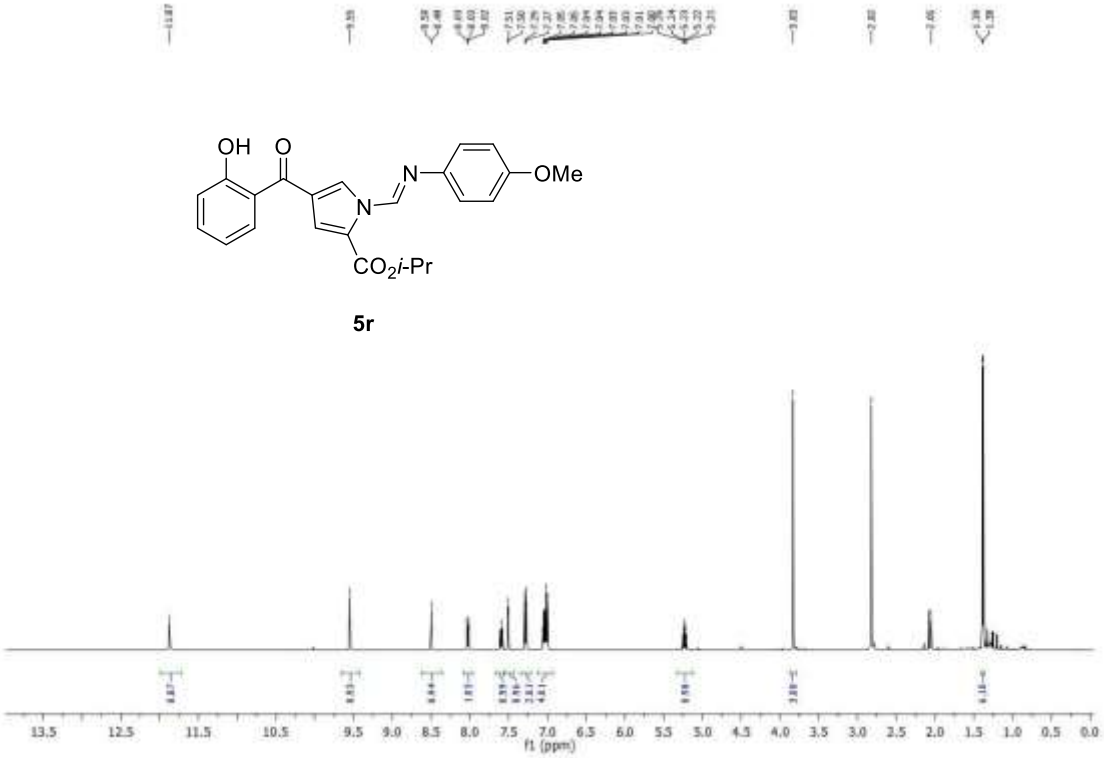
10
0
f1 (ppm)

5q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OMe
N
CO2i-Pr
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10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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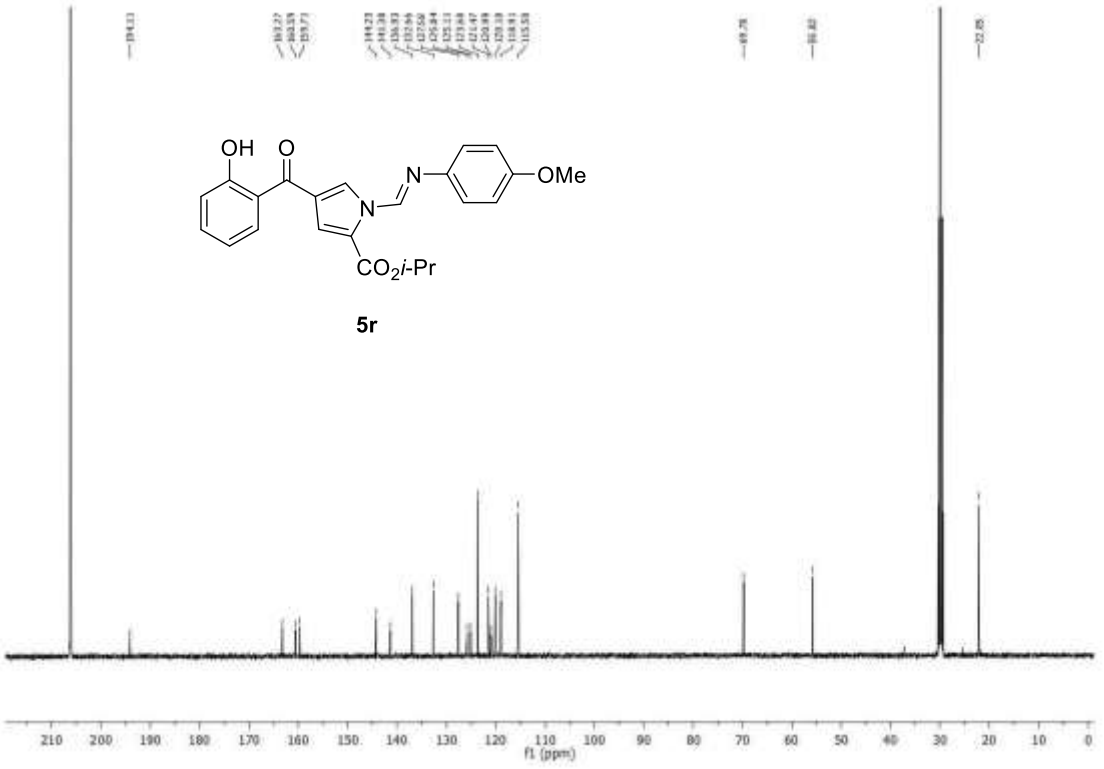
0.0
f1 (ppm)

5r


OH
O
N
OMe
N
CO2i-Pr
210
200
190
180
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40
30
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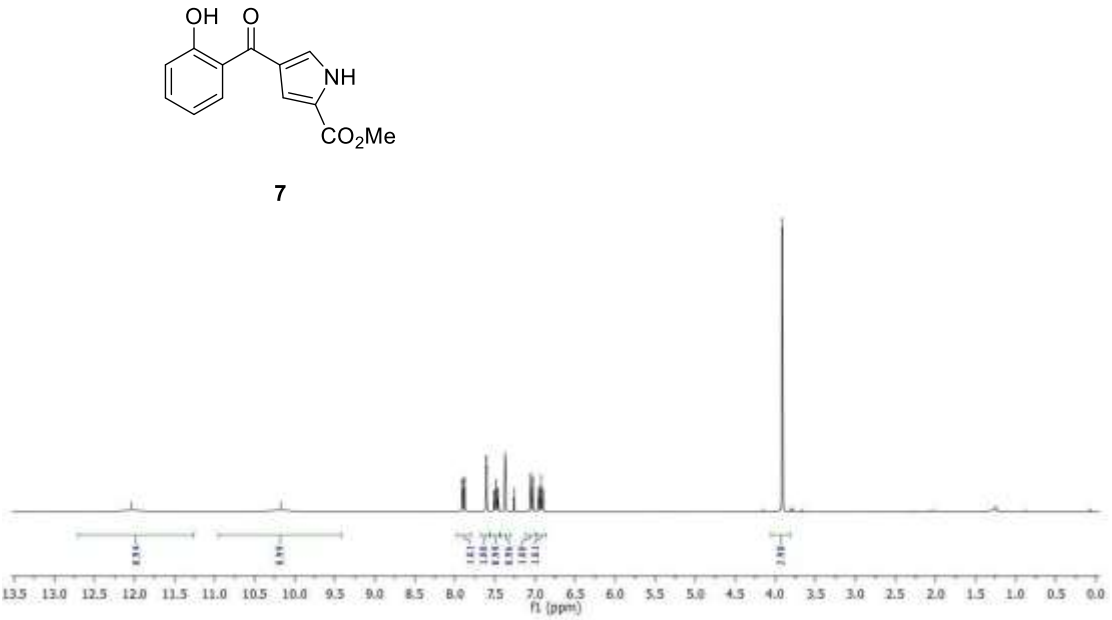
0
f1 (ppm)

5r


OH
O
NH
CO2Me
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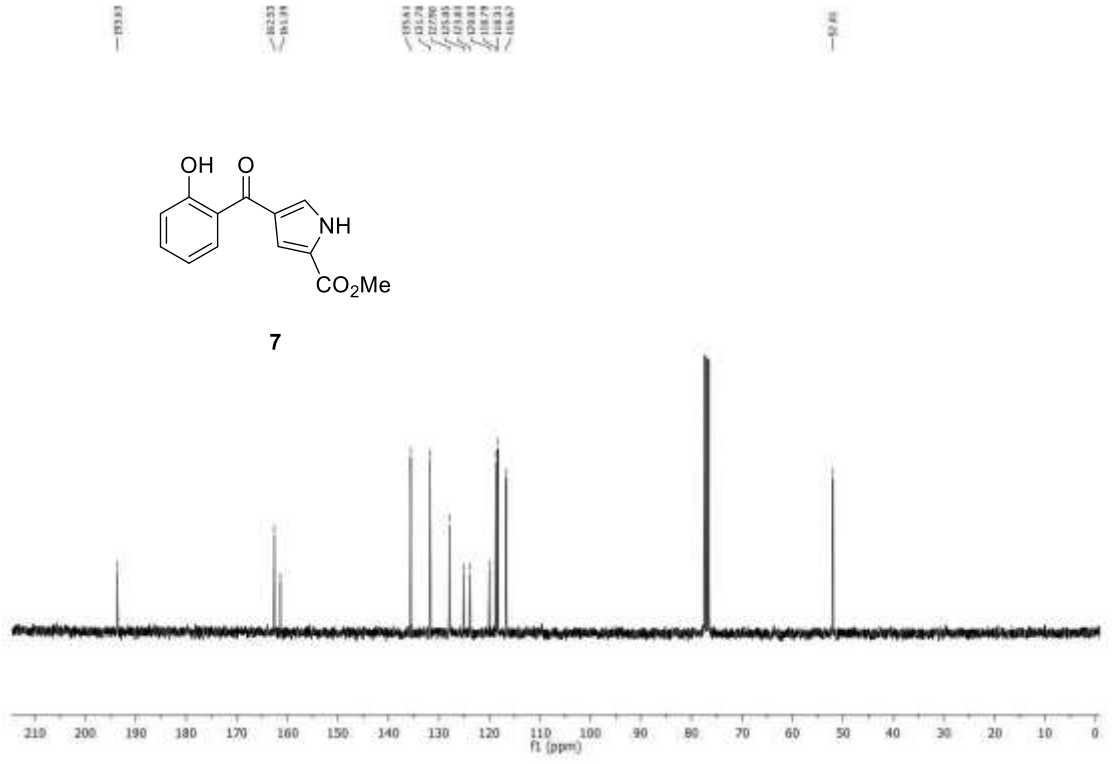
f1 (ppm)

7


OH
O
NH
CO2Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7

IX. DFT calculations

DFT calculations were performed with the Gaussian 09 programs.[3] All equilibrium structures and transition states (Tables S2 and S3) were fully optimized using M06-2X density functional method[4] together with the standard 6-31G* basis set. The M06-2X functional was chosen in this study as it is better suited in handling kinetics, thermodynamics and non-covalent interactions.[4-5] Frequency calculations were performed on the M06-2X/6-31G* optimized geometries to confirm the nature of the stationary points as equilibrium structures (with all the real frequencies) or transition states (with only one imaginary frequency). The identities of all calculated transition states were confirmed by intrinsic reaction coordinate (IRC) calculations. The effect of solvation was evaluated by SMD implicit solvation model[6] through M06-2X/6-311+G** single-point energy calculation, based on the gas-phase M06-2X/6-31G* optimized geometry. Relative Gibbs energies (ΔG) were computed at M06-2X/6-311+G**//M06-2X/6-31G* level in tetrahydrofuran (THF) solvent (ε = 7.58) at 298 K.

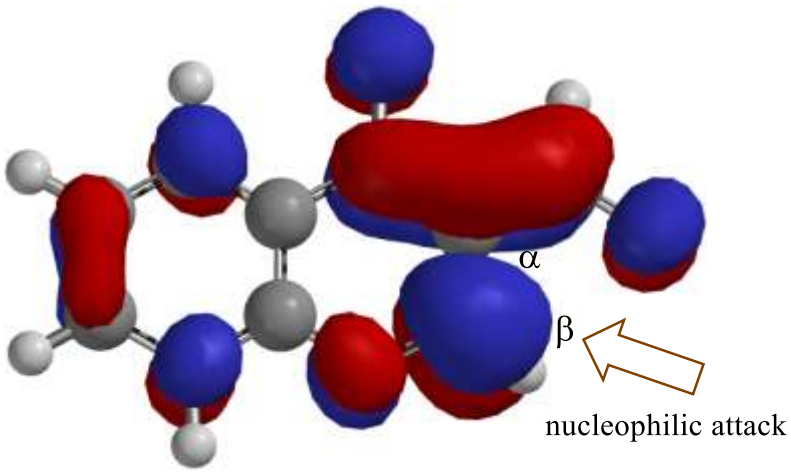


Figure S3. The lowest unoccupied molecular orbital (LUMO) of **1a**.

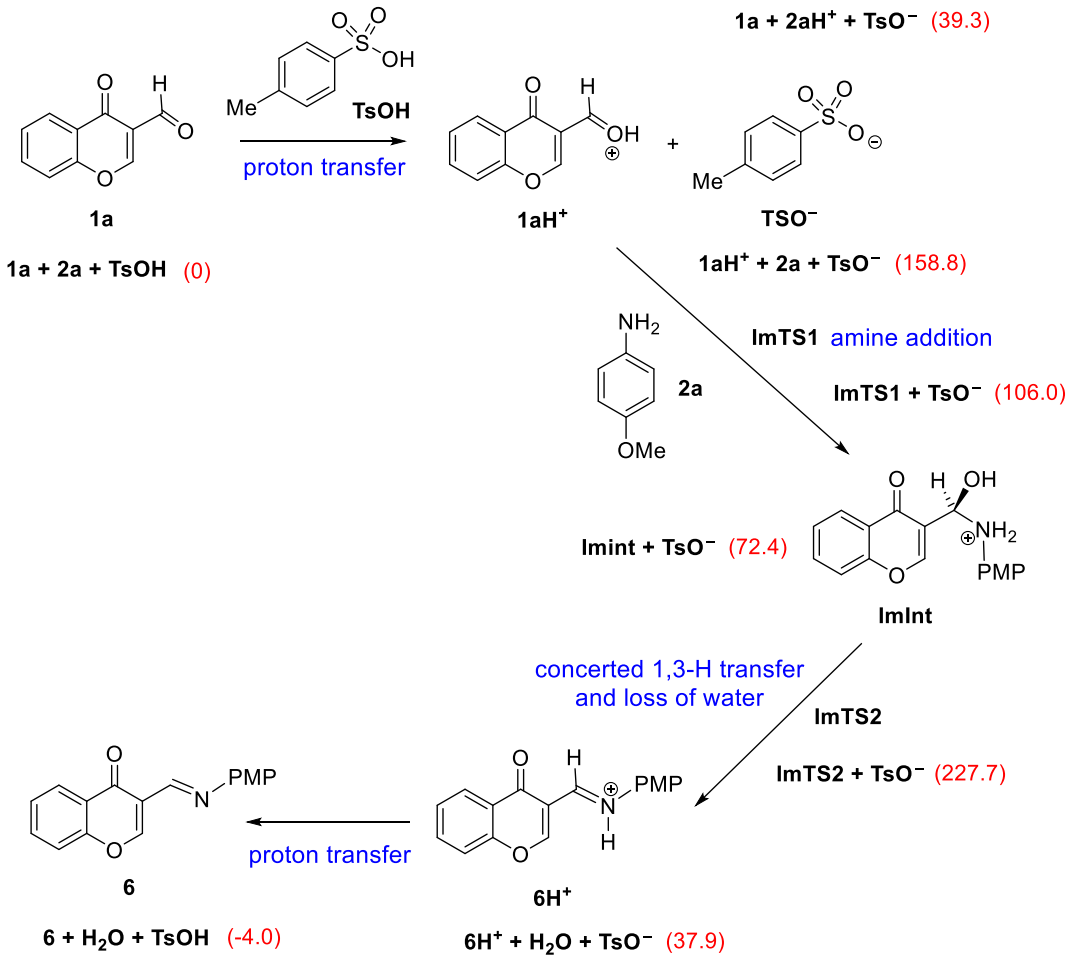


Figure S4. Computed reaction pathway of imine **6** formation under acidic conditions (TsOH) in THF. Relative Gibbs energies (ΔG_{298}, kJ/mol) are given in parentheses.

Table S2. Calculated electronic energies and number of imaginary frequencies for all M06-2X/6-31G* optimized structures.

Compound	Total energy (Hartrees)	No of Imaginary Frequencies
1a	-610.089839	0
1aH$^+$	-610.41271	0
2a	-401.94351	0
2aH$^+$	-402.30072	0
6	-935.65403	0
6H$^+$	-936.03100	0
H$_2$O	-76.37338	0
A	-1012.05531	0
B	-1012.06188	0

C	-1012.05079	0
TS1	-1012.03152	1
TS2	-1012.42152	1
TS3	-1012.36962	1
TsOH	-895.11546	0
TsO^-	-894.59411	0
ImTS1	-1012.42151	1
ImInt	-1012.43829	0
ImTS2	-1012.36962	1

Table S3. Cartesian coordinates of all calculated structures (M06-2X/6-31G*).

1a			
H	3.962828	-1.600738	0.000000
C	3.121469	-0.915900	0.000000
H	1.611005	-2.467489	0.000000
C	1.826622	-1.403388	0.000000
C	2.287241	1.358847	0.000000
C	0.738998	-0.522065	0.000000
C	3.347486	0.467404	0.000000
C	0.989551	0.850385	0.000000
C	-0.653515	-1.028846	0.000000
H	4.363392	0.849433	0.000000
H	2.433950	2.433408	0.000000
C	-1.662250	0.037498	0.000000
C	-1.289005	1.336241	0.000000
H	-2.011196	2.146640	0.000000
O	-0.029072	1.772308	0.000000
O	-0.928105	-2.216929	0.000000
C	-3.107510	-0.284977	0.000000
H	-3.341164	-1.363505	0.000000
O	-3.975715	0.559658	0.000000

2a			
C	-0.351573	0.108932	-1.850422
C	-0.248696	0.012102	0.961837
C	-1.526041	0.141404	-1.085221
C	0.866939	0.029440	-1.178686
C	0.925995	-0.018391	0.214536
C	-1.475314	0.092330	0.297099
H	-2.488525	0.211521	-1.585800
H	1.791955	0.010137	-1.749602

$1aH^+$			
H	4.008394	-1.582226	0.027159
C	3.162557	-0.904045	0.008147
H	1.671680	-2.476122	0.089237
C	1.869687	-1.409933	0.042962
C	2.313508	1.367233	-0.076823
C	0.780848	-0.535455	0.018403
C	3.381540	0.475944	-0.051352
C	1.036082	0.835427	-0.041122
C	-0.604389	-1.034115	0.053873
H	4.394711	0.862349	-0.078219
H	2.455499	2.441216	-0.122829
C	-1.637981	0.053209	0.019788
C	-1.244318	1.382637	-0.039479
H	-1.922398	2.234557	-0.067572
O	-0.013174	1.762579	-0.068327
O	-0.919767	-2.200826	0.105655
C	-2.969990	-0.365796	0.051216
H	-3.157933	-1.438755	0.097313
H	-3.933502	1.301295	-0.006985
O	-4.051735	0.334228	0.033935

$2aH^+$			
C	1.726093	-0.084470	-0.002791
C	-1.007415	0.275084	-0.015573
C	1.223239	1.213476	-0.050225
C	0.906145	-1.196567	0.038020
C	-0.474466	-1.019243	0.031718
C	-0.145614	1.387724	-0.056414
H	1.882072	2.077446	-0.081935

H	1.895479	-0.081035	0.695169
H	-2.383052	0.114908	0.891345
O	-0.310475	-0.032724	2.325390
C	0.910527	-0.105079	3.020367
H	1.467202	-1.015287	2.761396
H	0.657825	-0.127052	4.080927
H	1.541729	0.769537	2.815695
N	-0.405371	0.220540	-3.249868
H	-1.263273	-0.141644	-3.648016
H	0.394668	-0.189639	-3.716148

6

C	1.285328	-0.157022	-0.009508
C	2.211113	0.959053	0.227118
O	3.066181	-1.702952	-0.394849
C	3.638733	0.584699	0.121076
C	1.768217	-1.384823	-0.302994
C	4.002754	-0.727431	-0.182349
C	4.648874	1.533375	0.325121
H	1.120852	-2.234875	-0.490104
H	5.577154	-2.141120	-0.524151
C	5.979474	1.170437	0.226160
H	4.343886	2.548061	0.561280
H	6.759720	1.907041	0.385483
C	6.321211	-0.154937	-0.079514
H	7.365795	-0.439931	-0.156031
C	5.340155	-1.110066	-0.285709
O	1.843005	2.093697	0.487139
C	-0.160585	0.082306	0.078595
H	-0.444708	1.114514	0.312860
N	-1.003521	-0.859132	-0.091268
C	-2.380524	-0.562661	-0.042250
C	-5.144605	-0.113309	0.100325
C	-3.238689	-1.541740	0.478474
C	-2.934915	0.624793	-0.521669
C	-4.308015	0.855094	-0.455060
C	-4.599431	-1.316666	0.565010
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H	-2.293636	1.370029	-0.983363
H	-4.708271	1.782621	-0.847171
H	-5.272826	-2.059817	0.978814
O	-6.493272	0.008028	0.217443
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H	-6.683023	2.074325	0.316442
H	1.315690	-2.203198	0.074804
H	-1.117010	-1.889793	0.063664
H	-0.585431	2.378009	-0.092596
O	-2.310336	0.560616	-0.025831
C	-3.247021	-0.509525	0.013462
H	-3.132410	-1.157470	-0.861730
H	-4.228941	-0.040954	-0.003484
H	-3.132079	-1.091842	0.933583
N	3.200871	-0.272589	0.003899
H	3.641861	0.115697	-0.840609
H	3.442677	-1.270445	0.040369
H	3.642076	0.176355	0.817668

6H$^+$

C	1.320050	-0.258830	-0.083610
C	2.214395	0.899858	0.189083
O	3.139421	-1.708624	-0.523188
C	3.647724	0.577054	0.111148
C	1.854902	-1.464835	-0.443379
C	4.059634	-0.711375	-0.231959
C	4.625244	1.542690	0.377053
H	1.274264	-2.339936	-0.726117
H	5.668316	-2.082239	-0.590552
C	5.967123	1.207861	0.299903
H	4.297216	2.542698	0.642117
H	6.725371	1.954917	0.506443
C	6.349698	-0.094653	-0.045136
H	7.402252	-0.350799	-0.103532
C	5.398310	-1.068430	-0.316856
O	1.767574	1.999071	0.450354
C	-0.079612	0.011816	0.005388
H	-0.352173	1.060225	0.117689
N	-1.048277	-0.857377	-0.001418
C	-2.445103	-0.577341	0.012467
C	-5.174571	-0.083597	0.120691
C	-3.299941	-1.539964	0.560431
C	-2.948183	0.612383	-0.504879
C	-4.311855	0.866250	-0.444867
C	-4.654690	-1.293163	0.614934
H	-2.901778	-2.469793	0.958597
H	-2.293885	1.334207	-0.984430
H	-4.694451	1.791552	-0.857017
H	-5.344138	-2.015162	1.037380
O	-6.499169	0.059382	0.221307

H	-8.147504	1.116595	-0.037671
H	-6.914466	1.357745	-1.305093

H_2O			
O	0.001289	0.000000	0.000992
H	0.005546	0.000000	0.966465
H	0.935818	0.000000	-0.241518

A			
H	5.237707	0.470669	0.634509
C	4.342711	1.069451	0.495535
C	1.997377	2.525082	0.078696
C	3.167511	0.401755	0.141132
C	4.351355	2.446818	0.649554
C	3.174136	3.170046	0.434123
C	1.995821	1.137961	-0.063705
H	5.263946	2.961398	0.930904
H	3.173566	4.249786	0.550020
H	1.073109	3.067714	-0.088219
C	3.174456	-1.067983	-0.085069
O	4.214191	-1.707503	-0.112549
O	0.828862	0.546545	-0.450403
C	0.629253	-0.807859	-0.031107
H	0.375244	-0.782523	1.039040
C	1.842363	-1.667595	-0.279422
C	1.781665	-2.994544	-0.534974
O	0.691327	-3.734946	-0.691138
H	2.708065	-3.556528	-0.624115
N	-0.531176	-1.317172	-0.738074
H	-0.083268	-3.121195	-0.645736
H	-0.355131	-1.186761	-1.735220
C	-1.775406	-0.698848	-0.369329
C	-4.203241	0.461001	0.387193
C	-2.461579	-1.168746	0.753470
C	-2.310638	0.353032	-1.101150
C	-3.527606	0.929820	-0.739714
C	-3.658562	-0.588947	1.135968
H	-2.050456	-2.000818	1.318822
H	-1.766901	0.737190	-1.959837
H	-3.924296	1.744578	-1.333549
H	-4.206386	-0.940795	2.003480
O	-5.388495	0.949897	0.834277
C	-5.981906	1.995894	0.097653
H	-5.345725	2.889599	0.089446
C	-7.094518	1.259165	-0.254734
H	-6.699581	2.128444	0.281457
H	-8.159759	1.158475	-0.056484
H	-6.929409	1.374715	-1.331083
H	-0.813849	-1.848930	0.003822

TS1			
H	-6.125283	1.444197	-0.604284
C	-5.247356	1.672853	-0.007592
C	-2.944303	2.167759	1.492516
C	-4.243612	0.704257	0.046759
C	-5.111470	2.871917	0.677076
C	-3.956942	3.116359	1.426214
C	-3.101775	0.970247	0.801371
H	-5.896714	3.619359	0.631460
H	-3.844517	4.054062	1.961539
H	-2.033073	2.334645	2.057528
C	-4.395550	-0.595722	-0.680250
O	-5.367021	-0.804492	-1.399335
O	-2.052591	0.076463	0.875516
C	-2.261839	-1.196820	0.467573
C	-3.340283	-1.533507	-0.403005
C	-3.408821	-2.909684	-0.777216
O	-2.688588	-3.781687	-0.268564
H	-4.173660	-3.179717	-1.523893
N	-2.590401	-2.116537	2.030872
H	-2.706923	-3.046465	1.604600
H	-3.485239	-1.769618	2.375930
C	-1.530198	-2.050696	2.981976
C	0.642981	-1.837908	4.708598
C	-0.491379	-2.982234	2.909957
C	-1.469406	-1.005258	3.893896
C	-0.389930	-0.899536	4.767596
C	0.586610	-2.876254	3.770937
H	-0.538605	-3.785391	2.178337
H	-2.266724	-0.266918	3.926423
H	-0.366998	-0.084348	5.480493
H	1.402644	-3.589838	3.741241
O	1.735110	-1.828461	5.511690
C	1.834466	-0.795875	6.468770
H	1.864193	0.189668	5.988601
H	2.769224	-0.967698	7.001552
H	0.998926	-0.829438	7.178489
H	-1.309615	-1.704876	0.315109

H	-6.920977	2.224990	0.601150
H	-6.187404	1.688965	-0.935090

B

C	0.995674	3.986873	-2.433845
C	-1.092284	2.209814	-3.031363
C	-0.320359	4.276610	-2.002229
C	1.257753	2.778432	-3.092490
C	0.226168	1.903211	-3.383617
C	-1.350446	3.384994	-2.346712
H	2.281352	2.573493	-3.387038
H	0.444232	0.979952	-3.912343
H	-2.374291	3.645464	-2.096072
H	-1.904017	1.542253	-3.298527
C	-0.567584	5.531586	-1.245163
O	0.219702	6.480412	-1.350782
C	-1.728741	5.664630	-0.355132
C	-2.263652	4.579055	0.314390
H	-1.853937	3.584909	0.151254
C	-2.192857	7.011677	-0.059403
O	-3.136106	7.271191	0.682750
H	-1.643549	7.822977	-0.562971
N	-3.260925	4.656874	1.194551
H	-3.655508	5.594383	1.310832
C	-3.767574	3.588950	1.966632
C	-4.850804	1.507726	3.488240
C	-2.987383	2.472895	2.288994
C	-5.077432	3.662066	2.430047
C	-5.622429	2.632292	3.192487
C	-3.530125	1.439069	3.031059
H	-1.946536	2.421948	1.985580
H	-5.684829	4.528698	2.184794
H	-6.645159	2.718063	3.539402
H	-2.938728	0.567993	3.291528
O	-5.281208	0.445264	4.213266
C	-6.602373	0.485332	4.707608
H	-6.748963	1.336849	5.383206
H	-6.746775	-0.443380	5.259108
H	-7.331665	0.541111	3.890266
O	2.028158	4.815838	-2.231560
H	1.658610	5.669219	-1.910534

C

H	-4.253164	0.917521	2.167207

TS2

H	-2.696484	1.867884	1.527123
C	-2.970132	1.627436	0.504534
C	-3.615134	0.925992	-2.127100
C	-2.425301	0.463269	-0.053305
C	-3.821756	2.426093	-0.234916
C	-4.141989	2.069666	-1.553814
C	-2.755786	0.127608	-1.369041
H	-4.242977	3.326882	0.198875
H	-4.810280	2.696790	-2.135514
H	-3.847802	0.629537	-3.143992
O	-2.260159	-0.988930	-1.979476
C	-1.429472	-1.788575	-1.285418
H	-1.088623	-2.647397	-1.853313
C	-1.052154	-1.575532	-0.013518
C	-1.515290	-0.403821	0.720750
O	-1.164234	-0.159513	1.870511
C	-0.151242	-2.558956	0.664189
H	-0.603519	-2.858251	1.629381
N	1.217168	-1.886289	1.102625
H	1.297792	-1.753778	2.111464
C	1.676296	-0.739041	0.363184
C	2.516581	1.453295	-1.130956
C	2.005871	-0.898571	-0.977575
C	1.750736	0.519160	0.959266
C	2.176836	1.608227	0.217484
C	2.424859	0.195553	-1.730795
H	1.918578	-1.883573	-1.427113
H	1.448817	0.645402	1.994712
H	2.246822	2.597253	0.656904
H	2.680377	0.051884	-2.773633
O	0.393762	-3.534114	-0.082943
O	2.921509	2.580845	-1.769269
C	3.239863	2.476303	-3.139525
H	4.084413	1.795571	-3.302374
H	3.516761	3.479617	-3.462788
H	2.378467	2.129781	-3.723515
H	1.470423	-2.943268	0.586657

TS3

H	-4.956119	-1.007373	1.821846
C	-4.956757	-0.422150	0.907946
C	-4.865558	1.070966	-1.463542

C	-4.196098	1.001925	1.086394
C	-3.960804	1.170972	-1.697783
C	-3.120925	0.373278	0.444398
C	-5.137614	1.700079	0.353070
C	-5.015210	1.782202	-1.041979
C	-3.019573	0.468482	-0.944117
H	-5.969884	2.185334	0.851782
H	-5.753630	2.330858	-1.618222
H	-3.842512	1.220939	-2.774587
O	-1.993963	-0.113602	-1.634807
C	-1.070525	-0.815001	-0.953030
H	-0.308118	-1.222515	-1.608019
C	-1.062549	-0.993738	0.380950
C	-2.100669	-0.373297	1.215611
O	-2.115132	-0.450374	2.432981
C	-0.022459	-1.861074	1.051594
H	0.233388	-1.417802	2.023305
N	1.143241	-2.045241	0.195929
H	1.566664	-2.938301	0.429538
C	2.107647	-1.016840	0.102280
C	4.078186	0.972099	-0.193680
C	3.336717	-1.301251	-0.496289
C	1.878007	0.291155	0.551418
C	2.852099	1.268215	0.400957
C	4.319387	-0.327449	-0.641765
H	3.525492	-2.308208	-0.860287
H	0.938973	0.556682	1.025534
H	2.680788	2.281089	0.750350
H	5.260880	-0.595395	-1.107304
O	-0.544017	-3.131216	1.352549
H	-0.957278	-3.466089	0.541844
O	4.964888	2.004038	-0.289168
C	6.210430	1.728523	-0.884464
H	6.761996	0.962460	-0.324489
H	6.771086	2.663430	-0.864025
H	6.093842	1.397650	-1.924520

TsOH

C	-0.115474	0.065019	0.009161
C	1.217808	0.049555	-0.403696
C	1.948274	1.229174	-0.514261
C	1.323952	2.431139	-0.206457
C	-0.008175	2.482143	0.198438
C	-0.716539	1.294451	0.306898
C	-3.717067	-0.125011	0.321581
C	-6.125936	0.026270	0.325230
C	-6.075084	0.774112	-0.862089
C	-3.691385	0.616605	-0.860851
H	-7.084394	-0.200058	0.779865
H	-6.995969	1.123640	-1.318049
H	-4.800069	1.640515	-2.383887
O	-2.519103	0.912595	-1.491587
C	-1.365565	0.537993	-0.923118
H	-0.500648	0.813138	-1.516868
C	-1.252975	-0.119391	0.250818
C	-2.459115	-0.599122	0.915509
O	-2.443636	-1.380292	1.873247
C	0.150751	-0.359572	0.760657
H	0.473027	0.395751	1.485899
N	1.047786	-0.785811	-0.207829
H	0.683550	-1.991920	0.655167
C	2.349328	-0.272587	-0.163758
C	5.009179	0.697773	-0.203711
C	3.423420	-1.092674	-0.528634
C	2.648804	1.064816	0.158596
C	3.952828	1.537038	0.151163
C	4.734673	-0.623961	-0.553747
H	3.213407	-2.123787	-0.798189
H	1.841738	1.754744	0.396295
H	4.176709	2.569212	0.401918
H	5.529767	-1.303262	-0.840715
O	0.129861	-1.694969	1.585508
H	-0.806939	-1.981140	1.777752
O	6.257848	1.258895	-0.187625
C	7.328767	0.437432	-0.580144
H	7.438807	-0.428552	0.085910
H	8.226787	1.053496	-0.519445
H	7.204338	0.078728	-1.610318

ImTS1

H	-0.089723	-0.761770	-3.867032
C	0.683316	-0.000145	-3.875964
C	2.704929	1.948350	-3.823799
C	1.416816	0.208863	-2.699494
C	0.953588	0.753289	-5.003308
C	1.963359	1.726578	-4.973194
C	2.419584	1.180957	-2.698952
H	0.386430	0.593111	-5.913532

H	1.690567	-0.897870	-0.646733
H	2.980797	1.226353	-0.848453
H	-0.472808	3.439596	0.411586
H	-1.756291	1.316594	0.622567
C	-0.910063	-1.210135	0.119725
H	-1.703032	-1.239623	-0.634846
H	-0.276508	-2.088505	-0.022694
H	-1.388586	-1.288921	1.100700
S	2.241670	3.938778	-0.322818
O	3.482594	3.681817	-1.030819
O	1.341219	5.001882	-0.697105
O	2.647134	4.221453	1.222763
H	3.581438	3.969612	1.330370

TsO^-

C	-0.177103	0.030713	-0.002310
C	2.630516	0.012968	0.000730
C	0.521655	0.025791	1.201056
C	0.524173	0.040998	-1.204176
C	1.916122	0.032804	-1.199573
C	1.913521	0.016414	1.199555
H	-0.044551	0.051637	2.127492
H	-0.042267	0.076792	-2.129971
H	2.462241	0.048448	-2.141783
H	2.457541	0.018726	2.142958
C	4.139214	-0.031675	0.000244
H	4.508917	-1.060297	-0.093589
H	4.549090	0.379150	0.928340
H	4.555161	0.540103	-0.835886
S	-1.985614	-0.030716	0.000467
O	-2.292587	-1.470625	0.078957
O	-2.358932	0.733738	1.205740
O	-2.360704	0.602331	-1.278251

ImInt

H	0.292277	1.550457	-4.160570
C	1.351907	1.317461	-4.162499
C	4.092679	0.692486	-4.091928
C	1.917687	0.788290	-2.990902
C	2.142966	1.528222	-5.274309
C	3.511852	1.215219	-5.234924
C	3.282284	0.484343	-2.979299
H	1.709934	1.935258	-6.181204
H	4.126764	1.382294	-6.113116
H	2.172722	2.314149	-5.860906
H	3.495026	2.689476	-3.778602
C	1.144569	-0.573586	-1.485437
O	0.306220	-1.462925	-1.422191
O	3.190544	1.417131	-1.581420
C	2.964228	0.721077	-0.478414
C	1.986475	-0.205844	-0.335757
C	1.871557	-0.973341	0.948638
O	3.103986	-1.242188	1.556591
H	1.247432	-1.862813	0.811933
N	1.211576	-0.151473	2.057483
H	1.502597	0.825742	1.925979
H	3.676017	0.969558	0.305254
H	1.676534	-0.476038	2.916700
C	-0.258295	-0.213260	2.264242
C	-1.116117	-0.664017	1.278195
C	-0.725618	0.229971	3.502285
C	-2.486344	-0.682007	1.537032
H	-0.756121	-1.015944	0.315579
C	-2.081934	0.214573	3.753242
H	-0.039554	0.581700	4.269512
C	-2.976902	-0.243896	2.770298
H	-3.154301	-1.043108	0.765116
H	-2.482560	0.545276	4.704745
O	-4.270781	-0.225095	3.114699
C	-5.225264	-0.700200	2.176613
H	-6.192878	-0.609167	2.666624
H	-5.214181	-0.090877	1.266583
H	-5.036024	-1.749591	1.926815
H	3.600153	-1.878236	1.017448

ImTS2

H	-0.097588	1.006303	-4.263383
C	0.986388	0.956054	-4.254459
C	3.790036	0.798344	-4.147996
C	1.614819	0.477411	-3.095666
C	1.746973	1.347087	-5.339757
C	3.147007	1.266579	-5.282234
C	3.010155	0.407186	-3.063388
H	1.265664	1.717098	-6.238209
H	3.739093	1.575379	-6.137400
H	4.870028	0.728932	-4.082449
C	0.838172	0.059605	-1.926739
O	-0.384297	0.111882	-1.844840

H	5.145553	0.439323	-4.039931
C	1.113202	0.560554	-1.795135
O	-0.097248	0.816417	-1.740040
O	3.886049	-0.043001	-1.865519
C	3.166370	-0.272522	-0.777565
C	1.848020	0.014516	-0.650696
C	1.114728	-0.391791	0.603699
O	1.907462	-0.535926	1.720171
H	0.570008	-1.330810	0.468313
N	-0.000995	0.624895	0.884205
H	-0.392628	0.846488	-0.070158
H	3.759511	-0.740030	0.002585
H	0.421107	1.488786	1.243821
C	-1.047600	0.134966	1.787952
C	-2.237799	-0.305588	1.231486
C	-0.816980	0.081980	3.161396
C	-3.238020	-0.806304	2.059493
H	-2.396745	-0.255658	0.156690
C	-1.810404	-0.412169	3.984295
H	0.126323	0.415306	3.582075
C	-3.027181	-0.860017	3.442353
H	-4.169545	-1.141628	1.621085
H	-1.676385	-0.467810	5.058687
O	-3.921006	-1.316630	4.330196
C	-5.171048	-1.787583	3.849448
H	-5.726193	-2.106184	4.729739
H	-5.718847	-0.988729	3.338039
H	-5.033158	-2.638371	3.173556
H	2.566160	0.177773	1.752118

O	3.683214	-0.050947	-1.953908
C	3.002028	-0.453946	-0.889381
C	1.653524	-0.432292	-0.808805
C	0.883404	-0.922142	0.365452
O	1.828686	-1.120067	1.534039
H	0.333661	-1.851968	0.201249
N	0.076153	0.090144	1.041461
H	-0.015457	0.936672	0.477798
H	3.658443	-0.799708	-0.097776
H	1.220833	-0.247090	1.937117
C	-1.201548	-0.364666	1.573767
C	-2.268158	-0.628299	0.721290
C	-1.332024	-0.542341	2.951281
C	-3.474705	-1.081629	1.244145
H	-2.151367	-0.478249	-0.348539
C	-2.529264	-0.994645	3.476532
H	-0.510143	-0.290840	3.618461
C	-3.610673	-1.268568	2.625876
H	-4.299153	-1.281711	0.570892
H	-2.663984	-1.132424	4.543615
O	-4.729630	-1.699689	3.229088
C	-5.864478	-1.975872	2.423465
H	-6.646471	-2.293644	3.110705
H	-6.190074	-1.079156	1.885321
H	-5.652096	-2.780833	1.711373
H	1.650152	-1.949096	2.025785

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